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PRODUCTION OF AMINOACETONITRILE METAL CHAINS AND THEIR CATALYTIC EFFECTS

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PRODUCTION OF AMINOACETONITRILE METAL CHAINS AND THEIR CATALYTIC EFFECTS

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ABSTRACT. New experimental results regarding the following are reported: production of

aminoacetonitrile	acetate,
aminoacetonitrile	copper chains,
aminoacetonitrile	zinc chains in methanol,
aminoacetonitrile	nickel chains in methanol,
aminoacetonitrile	cobalt chains in methanol,

reactivity of $Cu(AAN)_2SO_4$ coordinators (reaction with formaldehyde, acetoaldehyde, acrylonitrile), catalytic action of metal chains in Sorbitol and glycerine oxydation. The experimental methods used are described.

Introduction

The nitrile radical has a coordination capability with respect to metals, /1* and coordinated compounds of mononitriles with inorganic chlorides have been known for a long time [1]. Recently, research has been undertaken on transition metal chains of Cu(I) [2], Ni(II) [3], Zn(II) [4] and others. There have already been reports on chains of saxinitrile and other polynitriles with Cu(I) [5], and $SnCl_4$, $TiCl_4$ [6]. There have also been many reports of alpha-amino acid metal chains, metal chains of alpha-amino acid amides, polypeptide metal chains and their catalytic action [7]. However, metal chains of alpha aminonitriles and their polymers, intermediate products of Strecker reactions which have amino radicals and nitrile radicals as the same carbon atoms, have not yet been reported. In our research, we succeeded in producing aminoacetonitrile metal chains. Alpha-aminonitrile is related to the production and function of the primitive protein substances involved in the origin of life, and the metal chains are also believed to have an important

*Numbers in the margin indicate pagination in the original foreign text.

function. We also anticipate polymerization and coordination and stabilization reactions of alpha-aminonitriles through the formation of chains. It may also be possible for them to have a catalytic action with regard to other compound reactions. In the free state, aminoacetonitriles are unstable, but their hydrochlorides, sulfates, etc., are stable, and in this study we succeeded in making aminoacetonitrile acetates from neutral sulfates. Chains were made from their reaction with metal ions, and their properties were investigated using infrared absorption spectra, etc. Next, we attempted to produce copper, /2 zinc, nickel and cobalt chains of aminoacetonitriles in nonaqueous solvents. Using copper aminoacetonitrile chains in an oxidation reaction through peroxide of polyhydric alcohols such as sorbitol, we examined their catalytic action.

OUTLINE OF EXPERIMENTAL RESULTS AND DISCUSSION

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Production of Aminoacetonitrile Acetate

$$CH_2=NH-CH_2-CN \xrightarrow{H_2SO_4} (NH_2CH_2CN)_2H_2SO_4 \xrightarrow{Ba(CH_3COO)_2} NH_2CH_2CN\cdot CH_3COO^-$$

When sulfuric acid reacted with methylene aminoacetonitrile (CH_2 = NH--CH_2-CN) aminoacetonitrile neutral sulfate was formed. A barium acetate solution was allowed to react with this, to yield aminoacetonitrile acetate. Aminoacetonitrile acetate has not yet been reported upon in the literature. Colorless crystals with a fusion point of 90-92.5°C are formed, and the element analysis values matched calculated values. Below we shall abbreviate aminoacetonitrile as AAN, and aminoacetonitrile acetate as AAN-AcOH.

Production of Aminoacetonitrile Copper Chains

Aminoacetonitrile copper chains are formed in water-ethanols, DMF (N,N-dimethyl formamide) and methanol. Table 1 shows the experimental results for the water-ethanols (1.5 by volume). Ethanol is added to solutions in various proportions of $CuSO_4$-$5H_2O$ and AAN-AcOH, and the sediment is separated

out. It is washed with methanol after filtering, and the material which is insoluble in methanol is the product. As shown in Table 1, the mixture proportions of $CuSO_4$-$5H_2O$ and AAN-AcOH are respectively: 1:0.5, 1:1, 1:1.34, 1:1.5, 1:2, 1:4 and 1:8. As the AAN-AcOH concentration rises, the analytical values of C, N increase gradually, and the copper value drops. For mixture /4 ratios of 1:4 or above, those values were more or less fixed. From these figures, a fixed experimental formula of $Cu(AAN)_2SO_4$ was found for the products in mixtures of 1:4 or more. Table 1-b shows the calculated analysis values for the various Cu-AAN chains. For mixture proportions of 1:2 or less, we were unable to find an experimental value indicating a fixed composition. For a mixture of 1:4 or more, those values are more or less fixed. The specific experimental formula of $Cu(AAN)_2SO_4$ was found from these figures for the products of a mixture of 1:4 or more. Table 1-b shows the calculated values for the various compositions of Cu-AAN chains. An experimental value showing the specific composition could not be found for mixtures of 1:2 or lower. When the AAN-AcOH concentration rises to a certain degree, since an experimental formula with a specific composition can be obtained, products of the mixture are assumed to be formed while the AAN is not sufficiently coordinated with the copper for these low mixture ratios. It is also assumed that the hydrogen analytical value is comparatively high, indicating the presence of water molecules. The color of the products is pale blue in mixtures of up to 1:1.5, blue for 1:2 and 1:4, amd pale blue for 1:8.

Table 2 shows the experiment results in DMF. The mixture ratios are 1:1, 1:2, 1:4, 1:8 for experiments numbered D-1 through D-4. All of these products are blue. For a mixture of 1:1, a product composition close to that obtained in 1:1.5 water-ethanol was obtained. For mixture ratios of 1:2 or more, products with the specific composition of $Cu(AAN)_2SO_4$ were obtained. For a mixture ratio of 1:8, only the copper value was slightly lower. Aside from the tendency of the copper value to drop when such a mixture ratio increases, the experimental results closely resemble those for water-ethanol.

Table 3 shows the experiment results in a methanol solution. The $CuSO_4$ /5 and AAN-AcOH mixture ratios in experiments numbered M-1 through M-5 are 1:1,

1:2, 1:4, 1:8, 1:10. For a mixture ratio of 1:1, a product with a composition almost the same as that formed in DMF is obtained. For a mixture ratio of 1:2, we obtained a product with a composition close to $Cu(AAN)_2SO_4$, but the copper value is somewhat low. As the mixture ratio increases from 1:4 to 1:8 and 1:10, the analysis values for C and N gradually rise, and there is a sharp drop in the copper value. This is believed to indicate the production of copper chains and three or more coordinated AAN molecules. When AAN is coordinated with Cu, AAN has a coordination capacity of up to four molecules if the amino radical only is coordinated, but products with 3 or 4 AAN molecules coordinated with the copper could not be isolated. For mixture ratios of 1:4 or above, mixtures of these chains are believed to be formed. The color of each of the mixtures is pale blue for mixture ratios up to 1:4, blue-green for 1:8, and blue-grey for 1:10. (For 1:10 both the $CuSO_4$ and the AAN-AcOH liquids were allowed to react for 30 minutes in a 60°C bath after mixing).

As seen from the above, the results obtained in methanol are rather different from those in water-ethanol or DMF. The difference from DMF is thought to be based on such properties as the dielectric constant of the catalyst, etc. However, the yield was almost the same for water-ethanol (1:4 or more), DMF (1:2 or more) or methanol (1:2 or more).

Figure 1 shows the products in a water-ethanol solution, and the infrared absorption spectrum of AAN-AcOH. The solid line shows that obtained by the /6 paste method, and the broken line shows that obtained by the KBr tablet method. The results are compiled in Tables 4-a and 4-b. The infrared absorption spectra by the paste method are considered. The 2250 cm^{-1} absorption in the AAN-AcOH is the nitrile absorption. It is broader than the usual nitrile absorption. For all of the products, the AAN-AcOH absorption is almost completely extinguished, and a new absorption is produced. For a mixture ratio of 1:0.5, the nitrile absorption is almost completely extinguished, while at 1:1, 1:1.34 it gradually begins to appear and after 1:1.5, there is a well-defined absorption. The two absorptions seen at 1660 cm^{-1} and 1590-1600 cm^{-1} show a intensity reversal as the mixture changes from

1:0.5 to 1:1, and the absorption in the vicinity of 1660 cm^{-1} becomes weak. When the mixture ratio is more than 1:4, the absorption is extinguished completely. While this absorption is extinguished, new ones arise at 1560 cm^{-1} and 907 cm^{-1}. The absorption at 1660 cm^{-1} which appears for products with low mixture ratios is thought to be the absorption for amide I, since they contain glycyl amide. In other words, part of the coordinated AAN is hydrolyzed by water of crystallization and changes into glycyl amide, thus, the nitrile absorption is weakened in these products. In mixture ratios of 1:4 or more, there is no glycyl amide content, and absorption occurs in the vicinity of 1660 cm^{-1} which coincides with the fact that the chains of $Zn(AAN)_2SO_4$, described later, do not reveal such absorption (in this case, even low mixture ratios contain no glycyl amide). These products in water-ethanol exhibit the /7
usual sulfate radical absorption at 1129-1114 cm^{-1}. There is sharp absorption in mixture ratios of 1:2 or more at 3330, 3250 and 3160 cm^{-1} which are thought to be expansion and contraction vibrations of the N-H in the coordinated amino radical [8]. From the above, the formation of AAN and $CuSO_4$ chains is clear. Nitrile absorption appears at 2250 cm^{-1} and the same location as for AAN-AcOH, with no marked shift. However, the absorption is slightly sharper. The absorption near 1600 cm^{-1} which appears in all products is thought to be due to the * vibration of $-NH_2$. Table 4-b shows the infrared absorption spectra using the KBr tablet method. Compared to the paste method, there are some differences in the intensity and location of absorptions, but there are no variations from the basic outlines given above.

Figure 2 shows the infrared absorption spectra by the paste method for the products in DMF. In this case, results analogous to those in water-ethanol were obtained. All of the products show N-H expansion-contraction vibrations at 3310, 3250 and 3160 cm^{-1}, nitrile expansion-contraction vibration at 2250^{-1}, and sulfate radical absorption at 1120 cm^{-1}. In this case, as well, there is an absorption at 1665-1653 cm^{-1} at low mixture ratios, which was found to be due to glycyl amide. Products with a mixture ratio of 1:1 show slightly different absorptions from those of other products. At 1:2 or more, as the absorption at 1653 cm^{-1} is lost, another is produced at 1570-1580 cm^{-1}. As a result, it is assumed that for 1:4 or more, the products obtained have /8

*Translator's Note: This is hand written in foreign text and almost illegible.

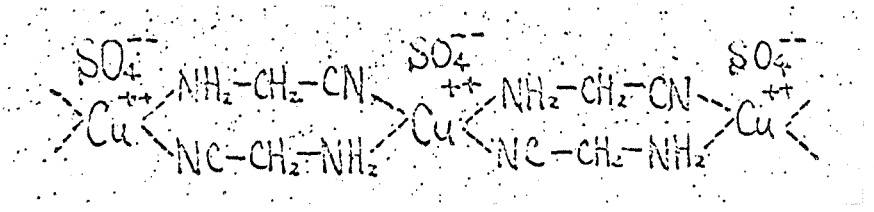
almost the same properties as those from water-ethanol at 1:4 or above. Figure 3 shows the infrared absorption spectra obtained by the paste method for products in methanol. As in the preceding two cases, there is N-H expansion-contraction vibration at 3310, 3270 and 3140 cm^{-1} and nitrile expansion-contraction vibration at 2250 cm^{-1}. There is also a strong sulfate radical absorption near 1110 cm^{-1}. At low mixture ratios, there is absorption at 1655 cm^{-1} which is assumed to be caused by glycyl amide. In the 1500-1700 cm^{-1} range, mixture ratios of 1:1, 1:2 have absorptions not only at 1655 cm^{-1} (amide I), but also at 1600 and 1565 cm^{-1} for 1:1, and 1610 and 1565 cm^{-1} for 1:2. There are also absorptions at 1600, 1560, 1530 cm^{-1} for 1:4, 1610, 1570, 1535, 1510 cm^{-1} for 1:8 and 1603, 1538 cm^{-1} for 1:10. At mixture ratios of 1:4 or more, (except for 1:10) these absorptions are more complex than those for products in water-ethanol or DMF, which may be due to the formation of products whose composition is different.

The 1600-1610 cm^{-1} absorption which is common to all of these is assumed to be due to deviation vibrations of $-NH_2$. As stated above, there was no striking shift in nitrile absorption in the infrared absorption for products in all of the solvents. In the past, a number of nitrile chains have been reported [1, 2, 3, 4], stating that, when the nitriles are coordinated, the absorption shifts in the direction of higher wave numbers. The greater the shift is, the stronger the coordination bond is. Because of this, it is /9
possible that the nitriles are not coordinated in the aminoacetonitrile copper chains described above. In view of the measuring instrument accuracy, the fact that nitrile absorption is sharper than for AAN-AcOH, the fact that copper II usually has 4 coordinators and 2 coordinators are unusual, etc., it is also possible that the bond is weak and the nitriles are coordinated with copper (II) ions. Figure 4 shows powder X-ray analysis patterns for reaction products in water-ethanol, which are summarized in Table 5. The value of d is calculated from $2d \sin \theta = n\lambda$ where $n = 1$. For a mixture of 1:1, a large peak is seen at $d = 13.37$. There is a peak at $d = 9.21$ for 1:2, and at $d = 9.72$ and $d = 9.21$ for 1:4. The patterns for 1:2 and 1:4 are comparatively similar. Almost identical results are found for 1:4 and 1:8.

Because of the fact that there is a large peak for the d value and no peak for copper sulfate, it is assumed there are at least two kinds of compounds of AAN coordinated with copper.

Table 6 shows the results of experiments on the recovery of coordinators for products in water-ethanol. All of the products are dissolved in a PH 3.25 citric acid soda buffer solution. Copper ions are not removed, and a given quantity is used to charge an amino acid analyzer. AAN and glycyl amide are isolated and measured. The AAN/Cu in Table 6 is the ratio of the number of moles of AAN and the number of copper atoms recovered. Gly-NH_2/Cu /10 indicates the same. (AAN+GlyNH_2/Cu) is the ratio of the combined AAN and GlyNH_2 to copper. 2(AAN+GlyNH_2)/total N is the ratio of the total number of nitrogen atoms obtained from the number of nitrogen atoms in the AAN and Gly-NH_2 recovered, and the atomic analysis value, multiplied by 100. It represents the nitrogen recovery rate. Its large value for mixture ratios of 1:0.5 is thought to be related to the small size of the nitrogen analytical value and the error. AAN and Gly-NH_2 are detected in mixture ratios of 1:2 or less, indicating that part of the coordinated AAN is hydrolyzed by water molecules in the product. This tendency becomes more pronounced, the smaller the mixture ratio is. For mixture ratios of 1:4 or more, Gly-NH_2 is not detected; the nitrogen recovery rate is close to 100% and the AAN/Cu value is close to 2. This is thought to indicate that 2 AAN molecules are coordinated with 1 copper ion, without changing into Gly-NH_2. Figure 5 shows the results of differential heat balance analysis in water-ethanol, and Table 7 summarizes the results. Mixture ratios 1:1 and 1:34 are similar, but rather different from 1:1.5, 1:2, 1:4, 1:8. The analysis results for 1:1.5, 1:2, 1:4 and 1:8 are rather similar. They are sharply exothermic at 140-150° C, with a simultaneous 2.2-4.5% weight loss. In proportion to the weight loss, this is very exothermic, and it is thought to be the reaction heat for condensation, polymerization, etc., between the coordinated AAN. For example, iminozation of the AAN occurs and part of the amino radicals turn to ammonia /11 and are separated. Such a change is not clearly evident in mixture ratios of 1:1 and 1:1.34. Since it occurs to a certain degree in products of coordinated AAN, there is little possibility that water of crystallization or the

like is separated. When these products are observed by means of an MP measurement device, they can be seen to turn black around 150° C. They are very endothermic from 230-370° C, with a weight loss of approximately 40%. Subsequently, there is a gradual loss in weight, and the total weight loss at 970° C is 60-70%. At 230-370° C, the sample is assumed to be broken down. If all the AAN is broken down here, the theoretical weight loss for 1:4 and 1:8 mixtures would have to be 59%, but the actual measured weight loss is 42-50%. Therefore, the AAN is not all isolated, but some of the nitriles may remain as cuprous cyanide. The fact that no step-by-step weight change like that of $CuSO_4 \cdot 5H_2O$ is exhibited appears to support this belief. The weight at 970° C is somewhat greater than CuO. With regard to chains with the composition $Cu(AAN)_2SO_4$ produced in water-ethanol or DMF, the AAN-C-C≡N bond is linear, and it is assumed to be impossible for the AAN to be coordinated with copper ions and form chelate rings. They are thought to have the following sort of structure. However, detailed structural questions such as whether the AAN is coordinated with the copper in cis- or trans- form remain to be solved by X-ray analysis.



Production of Chains from $CuSO_4 \cdot 5H_2O$ and $(AAN)_2H_2SO_4$ (Using Alkali).

A small excess of KOH is added to an aqueous solution containing $CuSO_4 \cdot 5H_2O$ and $(AAN)_2H_2SO_4$, and allowed to react below the freezing temperature of ice, yielding a reddish purple copper chain. Elementary analysis showed that these chains have the composition $Cu(AAN)_2(OH)_2H_2O$, but amino acid analysis showed no AAN. Only glycyl amide was detected. Thus, we found that $Cu(NH_2-CH_2-\overset{O}{C} = NH)_2$ chains were formed. This also corresponds with the fact that the chains exhibited no nitrile expansion-contraction vibration. The AAN is hydrolyzed by the excess alkali and converted to glycyl amide. This is coordinated with copper, and is assumed to form glycyl amide copper

chains. These chains are already formed from the reaction of glycyl amide and copper acetate [7].

Formation of Aminoacetonitrile Zinc, Nickel and Cobalt Chains in Methanol

Like the reaction of $CuSO_4 \cdot 5H_2O$ and AAN-AcOH in methanol, the reaction of metal ions with sulfate radicals such as $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, etc., with AAN-AcOH in methanol was found to produce a precipitate. The precipitate was examined. Table 8 shows the result of the reaction in methanol of $ZnSO_4 \cdot 7H_2O$ and AAN-AcOH. The mixture ratio of $ZnSO_4 \cdot 7H_2O$ to AAN-AcOH in Z-1 through Z-5 was 1:1, 1:2, 1:4, 1:8, and 1:10. The color was pale brown for 1:10, and white for the other mixtures. Aside from the 1:1 mixture, the yields were more or less identical. The products were slightly brown in the neighborhood of 170° C, and black-brown at around 205° C. For mixture ratios of 1:1, 1:2, 1:4, the products had a composition close to $Zn(AAN)_2SO_4$. However, for a mixture ratio of 1:4, the Zn value was rather low. For a mixture ratio of 1:1, 2 AAN molecules are coordinated with the zinc in the product, and the results were different from the copper sulfate case. In the 1:8 mixture, the analytical values for H, C, N are higher than for $Zn(AAN)_2SO_4$, and there is a tendency for 3 or more molecules of AAN to be coordinated with the Zn. In order to obtain chains with 3 or more AAN molecules coordinated with zinc in a 1:10 mixture, the reaction solution was heated at 60° C for 40 minutes after mixing, and the product was sufficiently rinsed in methanol. However, the product had the composition of $Zn(AAN)_2SO_4$ (the Zn value was somewhat low). Thus, those with 3 or more AAN molecules coordinated with zinc are assumed to be rather unstable and difficult to isolate. Even with a mixture ratio of 1:8, it is possible to obtain products with a composition of $Zn(AAN)_2SO_4$ if they are sufficiently rinsed with methanol. Just as in the case in which aminoacetonitrile copper chains are produced in methanol, as the mixture ratio rises, the analysis value of the metal drops in comparison with the H, C and N analysis values, but the reason for this is not clear.

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Figure 6 shows the infrared absorption spectra for these products. /14
The sharp absorption observed for all of the products at 3290, 3250, 3180 cm^{-1} is due to a N-H expansion-contraction vibration, while the sharp absorption at 2250 cm^{-1} is a nitrile expansion-contraction vibration. Moreover, the sulfate radical shows strong absorption at 1090 cm^{-1}. The absorption at 1595-1600 cm^{-1} is thought to be due to angular vibrations. For the 1:4 and 1:8 mixtures, there is an absorption at 1517 cm^{-1}. From amino acid analysis of the coordinators, we deduced that AAN, not converted into glycyl amide, is present, which corresponds to the lack of absorption in the neighborhood of 1650 cm^{-1}. Table 9 shows the results of reactions between $NiSO_4 \cdot 6H_2O$ and AAN-AcOH in methanol. The mixture ratios from N-1 through N-3 are 1:2, 1:6 and 1:8. The products are pale green, and the element analysis value is close to $Ni(AAN)_2SO_4 \cdot H_2O$. In other words, in this range of mixture ratios, it is unrelated to the ratio and yields a more or less constant product. Figure 7 shows the infrared absorption spectra of these products. The sharp absorptions observed at 3310, 3290, 3200 cm^{-1} are due to expansion-contraction vibrations, and the absorption at 2250 cm^{-1} is due to nitriles. The strong absorption at 1605 cm^{-1} is assumed to be from $-NH_2$ angular vibrations, and the absorption at 1110 cm^{-1} is assumed to be due to SO_4^{--}. Table 10 shows the results of reactions between $CoSO_4 \cdot 7H_2O$ and AAN-AcOH. The mixture ratios are 1:4 (c-1) and 1:8 (c-2). The element analysis values for the various products closely coincide with $Co(AAN)_2SO_4$, but the cobalt value is as low as 2%. However, /15
products close to $Co(AAN)_2SO_4$ are thought to occur.

Figure 8 shows their infrared absorption spectra (paste method). These spectra closely resemble those for the previous two cases. The sharp absorptions at 3350, 3300 and 3200 cm^{-1} are due to N-H expansion-contraction vibrations, that at 2250 cm^{-1} to nitriles, 1110 cm^{-1} to SO_4^{--}, and the absorption observed 1605-1610 cm^{-1} — to $-NH_2$ angular vibration. As discussed above, $Zn(AAN)_2SO_4$, $Ni(AAN)_2SO_4 \cdot H_2O$ and $Co(AAN)_2SO_4$ are produced. In the case of nickel and cobalt chains, even while the mixture ratio increases, there is no tendency toward an increase in the number of coordinations observed. These are usually 6-coordination metals. Even when nitriles are coordinated, there are 4 coordinations, and the properties of these chains need to be examined in

greater detail. (There are a considerable number of 4-coordination Ni chains present.)

Even in these zinc, nickel, cobalt aminoacetonitrile chains, no conspicuous shifts in nitrile absorptions were observed in the infrared absorption spectra. However, even in these cases, it was considered possible for nitriles to be weakly coordinated with the metals as in the case of copper chains.

Reactivity of $Cu(AAN)_2SO_4$ Coordinators

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In glycine copper chains, since the glycine amino radicals and carboxyl radicals are coordinated with copper ions, the methylene radicals are activated and are microalkaline. They are easily condensed with aldehydes, and there is a high yield of oxyamino acids [9]. We also expect that in $Cu(AAN)_2SO_4$ chains, if the AAN amino radicals and cyano radicals are coordinated with copper, the methylene radicals will be activated. We tested the reactions of acetoaldehydes and acrylonitriles with formaldehyde and AAN coordinated with copper.

a) Reaction with Formaldehyde.

First grade reagent formalin is added to $Cu(AAN)_2SO_4$ in the presence of microalkaline Na_2CO_3, and it is allowed to react in a sealed tube (3 hours at 80° C). The reaction product was suitably diluted and analyzed in an automatic amino acid analyzer. Figure 9-I shows a chromatogram of it. AAN, NH_3 and Gly-NH_2 peaks appear. The peaks which appear after 107 minutes are hydrolyzed yielding serine, and are thus assumed to be $\begin{matrix} HOH_2C \\ H_2N \end{matrix}\!\!>\!CH\text{-}CN$.

Figure 9-II shows the chromatogram for a product resulting from a 3-hour reaction at 50° C and subsequent hydrolization. There are peaks for serine and glycine. From the fact that serine is produced, we found that formaldehyde is condensed with the AAN methylene radical. In this case, there is

9.8% serine and 18.8% glycine with respect to the AAN. The small total amount is thought to be due to incomplete hydrolization.

b) Reaction with Acetoaldehyde. /17

As in the case of formaldehyde, acetoaldehydes are added to the chains and allowed to react in a closed tube in the presence of microalkaline Na_2CO_3 (3 hours at 50° C). After hydrolysis, it is analyzed. Figure 9-III shows the chromatogram, with a threonine peak after 49 minutes. This fact indicates that the AAN methylene radical is condensed with the acetoaldehyde. The proportion of threonine produced with respect to the AAN in the chains is 65.2%; glycine is 9.5%. The condensation of acetoaldehyde on the above methylene radicals is assumed to proceed with a good yield.

c) Reaction with Acrylonitrile.

Acrylonitrile is added to an activated methylene radical forming a cyanoethyl compound. A great excess of acrylonitrile is added to $Cu(AAN)_2SO_4$, which is allowed to react in a closed tube in the presence of a microalkali or a microacid (3 hours at 80° C). The reaction product is hydrolyzed and then analyzed. Figures 10-I and 10-II show the results. As seen from the figures, no glutamic acid is produced in the product. This fact indicates that acrylonitriles are not added to the AAN. Other ninhydrin reaction positive materials are produced.

(1) $H_2N-CH_2-CN + HCHO \xrightarrow{OH^-} NH_2-\underset{\displaystyle CH_2OH}{CH}-CN \left(\xrightarrow{\text{hydrolysis}} \text{Serine}\right)$

(AAN coordinated with Cu)

(2) " $+ CH_3CHO \xrightarrow{OH^-} NH_2-\underset{\displaystyle CH_3-CH-OH}{CH}-CN \left(\xrightarrow{\text{hydrolysis}} \text{Threonine}\right)$ /17

(3) " $+ CH_2=CH-CN \xrightarrow[\text{or microacid}]{OH^-} NH_2-\underset{\displaystyle CH_2CH_2-CN}{CH}-CN \left(\xrightarrow{\text{hydrolysis}} \text{Glutanic acid}\right)$ /18

Summarizing the above, reactions 1 and 2 occur, while reaction 3 does not. Reactions 1 and 2 may become industrial methods of producing oxyamino acids from AAN.

Study of Catalytic Action of Metal Chains in Oxidation of Sorbitol and Glycerine

a) Catalytic Action in Oxidation of Sorbitol by H_2O_2 (Using D-Sorbitol).

Sorbitol is oxidized using hydrogen peroxide, and comparative studies were made of the catalytic action of $FeSO_4$, $CuSO_4$, $Cu(AAN)_2SO_4$, $Cu(CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2)_2 \cdot H_2O$, etc., with respect to the oxidation reaction. We prepared 1 M-sorbitol aqueous solution, approximately 1 M-H_2O_2 aqueous solution, 0.1 M-catalytic aqueous solution, and prepared 5 ml sorbitol solution; 5 ml H_2O_2 solution and 2 ml catalytic solution were added to produce a reaction solution. It was allowed to react for a long period of time at room temperature. Paper chromatography was first used to ascertain the products, but this method could not give adequate separation of the products. We next attempted to separate the products and sorbitol by means of gas chromatography. Polyhydric alcohols and sugars have a high boiling point and analysis by gas chromatography is difficult, but analysis is possible after conversion to trimethyl silyl ether for a derivative with a comparatively low boiling point [10]. In this method, the trimethyl silyl ether of polyhydric alcohol or sugar is dissolved in anhydrous pyridine with which a suitable amount of hexamethyl disilazane and /19
trimethyl chlorsilane is allowed to react. First, the D-glucose, D-sorbitol, L-sorbose, and other standard materials included in the reaction products are converted to trimethyl silyl ether (TMS), and then the gas chromatography conditions were examined. A hydrogen flame ionization detector was used as the gas chromatography detection device. The carrier used was a 60-80 mesh chromosorb W and the column was a 3 m or 1.8 m glass column (inside diameter, 4 mm). The fixed phase used was P.E.G. (Polyethylene glycol) 1500, 4000, H.V. silicone grease, SE-30 (methyl silicon polymer), etc. The fixed phase concentration was about 10% for polyethlene glycol, and about 5% for silicone

grease and SE-30. If the fixed phase concentration were too low, tearing occurred or peaks did not arise. Even with a PEG 1500 fixed phase concentration of 10%, there was tearing with TMS-sorbitol. The TMS-D-glucose chromatograms showed two peaks. Ordinary D-glucose had two peaks. In the silicone group fixed phase, the alpha body is known to be effluent earlier than the beta body, so the first peak is assumed to correspond to the alpha body, and the second peak — to the beta body. TMS-sorbitol, TMS-D-fructose, etc., all showed one peak each. TMS-L-sorbose had both a comparatively large peak and a small one. In the references [10], TMS-L-sorbose has one peak and when a second occurs, this is assumed to be due either to impurities in the sample or to TMS conversion conditions.

Figure 11 shows the chromatogram obtained under conditions of 175° C /20
column temperature, 6% SE-30, 3 m column, and nitrogen flow speed of 40 ml/min. The alpha-D-glucose and L-sorbose are isolated. The same isolation was obtained, as shown in Figure 12, for 5% H.V. silicone grease, 3 m column (column temperature 180° C, nitrogen flow speed 20 ml/min). The retention time for the various TMS materials obtained under these conditions, and the retention time for alpha-D-glucose used as a basis for comparison, are shown in Table 11. Next, the metal and water components were removed from the oxidation products of sorbitol, which were then TMS-ized and analyzed by gas chromatography. Figure 13 shows the case of a $FeSO_4$ catalyst (Fenton reagent) with a rather large peak from an unknown substance. D-fructose, alpha-D-glucose, beta-D-glucose are also produced, and a rather large amount of sorbitol remains. Figure 14 shows the case of a $CuSO_4$ catalyst. L-sorbose is produced, and the other products resemble those in the case of the $FeSO_4$ catalyst. Figure 15 shows the case of $Cu(AAN)_2SO_4$ chains as catalysts. The products are the same as in the case of the $CuSO_4$ catalyst, and no oxidation selectivity occurs as a result of chain formation. Figure 16 shows the case of a $Cu(NH_2CSC{=}NH)_2 \cdot H_2O$ catalyst, where there is almost no oxidation, but some alpha and beta D-glucose is produced. The product was evaluated by mixing a standard TMS material with the TMS material in the product, and observing where the peaks overlapped. If we compare the four types of

catalysts described above, we find that $Cu(NH_2CH_2C(=NH)_2)_2 \cdot H_2O$ has very little catalytic effect on oxidation. The catalytic action of the remaining three /21
are very similar, differing in that $CuSO_4$ and $Cu(AAN)_2SO_4$ produce L-sorbose, while $FeSO_4$ does not.

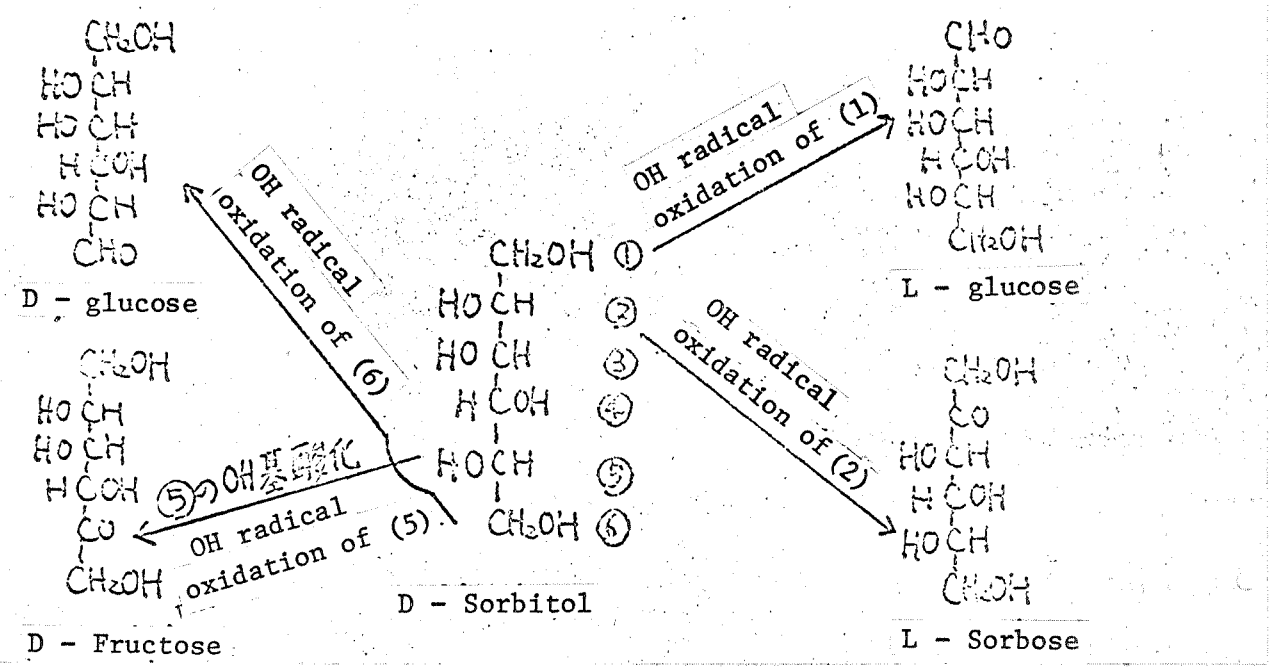


Figure 17 shows the relationship between the product and the position of the oxidized OH radical of the sorbitol. In the experiments described above, the oxidation products D-glucose, D-fructose, L-sorbose were observed. From Figure 17, it is possible that the peak for the unknown material may correspond to L-glucose. Based on the chromatograms of the various oxidation products, there is thought to be very little disruption of the C-C bonds.

b) Glycerine Oxidation Reaction.

When glycerine is oxidized, it is possible to obtain glycerine aldehyde or dihydroxyacetone. We first examined the gas chromatograms of glycerine, glycerine aldehyde and dihydroxyacetone after TMS-ization. In a 6% SE-30 3 m /22
column, TMS-glycerine aldehyde showed 2 peaks, one of which overlapped with

the dihydroxyacetone peak. The two could not be isolated. After they were oximized, attempts were made to isolate the acetylized or TMS-ized materials using 6% SE-30, 15% EGS-polyester (3 m column), etc., but they were not successful. However, oximized and TMS-ized ones were isolated, as shown in Figure 18, by 10% polyethylene glycol 4000, 3 m column. Figure 19 shows the isolation of TMS-ized glycerine, glycerine aldehyde oxime, dihydroxy acetone oxime.

Glycerine oxides were oximized or TMS-ized and analyzed by gas chromatography. Figure 20 shows the case of a $FeSO_4$ catalyst (Fenton reagent). Glycerine aldehyde and dihydroxyacetone are produced, but a great deal of dihydroxyacetone is produced. Figure 21 shows the case of a $CuSO_4$ catalyst, where there is more glycerine aldehyde than dihydroxyacetone produced.

The results with a $Cu(AAN)_2SO_4$ catalyst are the same as those with $CuSO_4$.

EXPERIMENTAL SECTION /78

Production of Aminoacetonitrile Acetate

a) Production of Methylene Aminoacetonitrile.

650 g (7.56 mol) HCHO and 216 g (4.00 mol) NH_4Cl are put into a round-bottomed vessel and kept at 0° C or lower. Meanwhile, a solution of 196 g (3.92 mol) NaCN in 650 cc deionized water is titrated. Titration is carried out in such a way that the temperature of the reaction system does not exceed 5° C. When about half of the total NaCN solution is titrated, the NH_4Cl is completely dissolved. At this time, titration of glacial acetic acid begins, continuing in such a way that titration of both NaCN solution and glacial acetic acid ends at the same time. Immediately after titration of glacial acetic acid begins, white crystals begin separating. After titration of both liquids is completed, they are agitated for about 2 hours to conclude the reaction. After filtration, the crystals are transferred to a beaker. 250 cc deionized water is added, agitated, and the solution is rinsed in deionized water after filtration. Recrystallization is accomplished by solution in 80° C deionized water.

Yield	95.5 g	Yield with respect to NaCN	36%
M.P.	131° C (Ref. value 129° C)	Colorless specular crystals	

b) Production of Aminoacetonitrile Neutral Sulfate [$(AAN)_2H_2SO_4$].

Methylene Aminoacetonitrile $\xrightarrow{H_2SO_4}$ $AAN \cdot H_2SO_4$ $\xrightarrow{BaCO_3}$ $(AAN)_2H_2SO_4$ /78

Previously, aminoacetonitrile neutral sulfate was produced as shown above, but in these experiments it was produced directly by adding sulfuric /79

acid to methylene aminoacetonitrile. Dense sulfuric acid 25.5 g (approximately 0.25 mol) is added to 125 cc 99% EtOH. The temperature of the solution rises, but it is adjusted to 65-70° C, and crystals of methylene aminoacetonitrile 34 g (0.5 mol) are added gradually. In the beginning, the methylene aminoacetonitrile dissolves, but after a certain point it ceases to dissolve. In an aqueous solution, this is heated for 1 hour (65° C) and then kept refrigerated overnight. The products are filtered and rinsed in a small quantity of ethanol, then dissolved in 100 cc deionized water. The undissolved material is filtered out (assumed to be unreacted methylene aminoacetonitrile). 99% EtOH (600 cc) is added, and crystals are separated. The products are obtained after one night's refrigeration. Recrystallization is performed by water-EtOH.

Yield 38%. M.P. 160° C (Ref. value 165° C)

Element Analysis Results

	Analysis Value	Calculated Value
H	4.80	4.79
C	22.53	22.85
N	26.44	26.65

c) Production of Aminoacetonitrile Acetate (AAN-AcOH)

28 g (0.133 mol) $(AAN)_2H_2SO_4$ are dissolved in 56 cc deionized water. Glacial acetic acid (0.266 mol) is added to 4.2 g (0.133 mol) $Ba(OH)_2 \cdot 8H_2O$ and dissolved. Then 26 cc deionized water are added. When the two liquids above are mixed, $BaSO_4$ precipitate is produced in large quantities. When approximately 30 cc deionized water is added and agitated well, the $BaSO_4$ is completely precipitated. The $BaSO_4$ is removed by a centrifugal separator (40 minutes at 7500 rpm). The reaction liquid obtained is light brown in color, with a pH of approximately 5.0. It is concentrated in a vacuum at a

/80

bath temperature of 40° C using a rotary evaporator. From time to time, ethanol is added to speed up the concentration rate. As concentration continues, a black product is ultimately separated out. This is thought to be a mixture of colorless acetate and black-brown AAN polymers. Thirty cc 99% EtOH is added, dissolving these black-brown impurities, which are removed by decantation. Next, 100 cc 99% etOH is added to dissolve the acetate at 60° C, and it is filtered after activated charcoal processing. If the filtrate is refrigerated overnight, colorless crystals are separated out. After filtration, it is rinsed with a small amount of cold ethanol and dried.

M.P. 90-92.5° C Yield 9.1 g Rate 29.4%

Element Analysis Results

	Analysis Value	Calculated Value
H	6.90	6.89
C	41.32	41.38
N	24.14	24.14

The reason that the yield is rather poor is that the boiling point of acetic acid is 118° C, close to that of water, so the acetic acid in the vacuum pump during condensation gradually evaporates, and aminoacetonitriles are produced, which change into black-brown materials due to polymerization and other reactions. The higher the bath temperature is during condensation, the lower the yield rate of $Ba(OH)_2$.

Production of Aminoacetonitrile Copper Chains /81

a) Production in Water-Ethanol Mixture Catalyst Systems.

An aqueous solution of 0.01 mol/50 cc $CuSO_4 \cdot 5H_2O$ is prepared, to which are added the following concentrations of AAN-AcOH solutions: 0.005, 0.01, 0.0134, 0.015, 0.02, 0.04, 0.08 mol/50 cc concentrations, in order of experiment

number. As the two liquids are mixed, the blue color of the solution becomes darker. To these mixed solutions, 500 cc 99% EtOH is added and chains are separated out. Under these conditions, AAN-AcOH is not separated, but a considerable amount of copper sulfate may be separated out. However, powder X-ray analysis showed no admixture of copper sulfate in these products. About 20 minutes after separation of the chains, they were filtered, rinsed 3 times in 60 cc methanol to yield the materials which were insoluble in methanol. The smaller the ratio of copper sulfate to AAN-AcOH, the greater the methanol-soluble content, and the rinsing liquid appeared bluish. If the mother liquor is let stand for several days, an excessive amount of AAN-AcOH is found in the mother liquor.

b) Production in DMF.

We dissolve 0.005-0.0025 mol $CuSO_4 \cdot 5H_2O$ in 25-15 cc DMF. Similarly, 0.005-0.02 mol AAN-AcOH are dissolved in 20-10 cc DMF. When both liquids are /82 mixed in various proportions, a bluish precipitate is produced. It is filtered and adequately rinsed with methanol, then suction dried by a vacuum pump. At a bath temperature of 65° C, suction is applied by a vacuum pump for approximately 4 hours.

c) Production in Methanol.

0.005-0.0025 mol $CuSO_4 \cdot 5H_2O$ is dissolved in 10-25 cc methanol, and 0.025-0.05 mol AAN-AcOH is similarly dissolved in 10-30 cc methanol. When both liquids are mixed in various proportions, a precipitate is produced. They are filtered by a glass filter, rinsed in methanol, and dried.

Production of Chains from $CuSO_4 \cdot 5H_2O$ and $(AAN)_2H_2SO_4$ (Using Alkali)

2.52 g (0.012 mol) $(AAN)_2H_2SO_4$ is dissolved in 10 cc deionized water. Then 2.49 g (0.01 mol) $CuSO_4 \cdot 5H_2O$ is dissolved in 10 cc deionized water, and

both liquids are mixed. While they are refrigerated below the freezing point of water, 3.92 g (0.07 mol) aqueous solution of KOH is titrated. When the KOH is titrated, a bluish precipitate is produced. Next, while agitating during refrigeration, the reaction is allowed to continue for approximately five hours. When the reaction is completed, the K_2SO_4 is removed by filtration. To the filtrate is added 120 cc 99% EtOH, and the unreacted $(AAN)_2SO_4$, $CuSO_4$ and K_2SO_4 are separated out. The filtrate is dark reddish-purple. After being kept as is overnight in the refrigerator, reddish-purple crystals are separated. The crystals are filtered, rinsed and dried. The yield was a very low 0.4457 g. Element analysis gave a formula of $Cu(AAN)_2(OH)_2 \cdot H_2O$ for this material, but amino acid analysis showed only glycyl amide coordinators, with no AAN detected at all. Since the molecular formula $Cu(AAN)_2(OH)_2 \cdot H_2O$ /83 completely coincides with $Cu(NH_2CH_2\overset{O}{C}{=}NH)_2 \cdot H_2O$, the chains produced in the above experiments were found to be glycyl amide copper chains.

Production of Zinc, Nickel and Cobalt Aminoacetonitrile Chains in Methanol

$ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, or $CoSO_4 \cdot 7H_2O$ acetoaminonitriles were dissolved by heating in methanol and mixed with methanol solutions of AAN-AcOH in the various mixture proportions shown in Tables 8, 9, and 10. The precipitated product was filtered, rinsed in methanol, and dried by a vacuum pump.

ANALYSIS

The C, H and N content of the reaction product was found by element analysis. /84

Determination of Metallic Ions: Metallic ions were found from chelate titration with 0.01 M-EDTA or from calculating the amount of ash from element analysis. A given amount of copper wire is dissolved in concentrated nitric acid, and a certain dilution, a metallic ion standard solution is prepared. A 0.01 M-EDTA standard solution was standardized. The various chains were difficult to dissolve in near neutral deionized water, so they were dissolved in a pH 4 buffer solution of acetic acid — soda acetate. After appropriate dilution, a given amount of buffer solution is added and titrated.

Copper: Approximately 0.05 of a sample chain is dissolved in 10 cc of acetic acid — soda acetate buffer solution. It is diluted with 100 cc deionized water, and 25 cc methanol is added. It is then titrated using PAN as the indicator.

Zinc: Approximately 0.05 g of a sample chain is dissolved in 2 cc of acetic acid — soda acetate buffer solution. It is diluted to 100 cc, and 4 cc of a pH 10 NH_3-NH_4Cl buffer solution is added. It is titrated using a BT indicator.

Nickel: To a sample solution of approximately 0.05 g, deionized water is added to dilute it to 100 cc. 10 cc of NH_3-NH_4Cl buffer solution is added, and a MX indicator is used. The pH is brought close to neutral using ammonia water, and it is titrated. The MX indicator is also used in the case of cobalt. It is neutralized with 1 N-ammonia water and titrated.

Infrared Absorption Spectrum: A Shimazu IR-27 was used. Wave number 4000 - 650 cm^{-1}. Nujoru paste or KBr capsule methods were used. /85

Analysis of Coordinators in Chains: Using Shibata Automatic Amino Acid Analyzer AA-600. Strong acid ion exchange resin Amberlight GC 120 was used. Column temperature 30° C, Column length 50 cm. Two buffer solutions used — one with pH 3.25, one with pH 5.28. One hour after analysis started, we changed to pH 5.28. Buffer solution flow rate, 0.2 ml/115 sec. Alternatively, a globular resin was used with buffer solution flow rate of 0.2 ml/75 sec. 0.5 hours after analysis started, buffer solution was changed to pH 5.28.

Differential Heat and Thermal Analysis: Rigaku Electric Automatic Differential Heat Balance used. Rate of heat increase 5° C/min or 10° C/min. Standard reagent: alpha-Al_2O_3. In atmospheric N_2(0.15 ℓ/min). Temperature range, 0-1000° C.

Powder X-Ray Analysis: Rigaku Electric X-Ray Diffractometer used. Current 10 mA. Voltage 30 kV. Full scale 3000 Count. TC 1.

$Cu(AAN)_2SO_4$ Chain Coordination Reactions

/86

a) Reaction with Formaldehyde:

0.0420 g $Cu(AAN)_2SO_4$ chains are dissolved in 0.5 cc citric acid soda buffer solution. 0.25 cc of 1 M-Na_2CO_3 aqueous solution is added. The pH of the solution is around 10. 1 cc formalin (1^{st}-class reagent) is added, and it is placed in a sealed tube. It is allowed to react for 3 hours in a vessel having 50° C constant temperature. When the reaction is completed, the tube is opened and with a 6 N-HCl aqueous solution it is hydrolyzed for 6 hours under a reflux. It is diluted to a total of 50 cc, and the product is analyzed by an automatic amino acid analyzer. The same solution allowed to react for 3 hours at 80° C is analyzed without being hydrolyzed. The standard serine material used was L-serine.

b) Reaction with Acetoaldehyde:

0.0392 g $Cu(AAN)_2SO_4$ is dissolved in pH 5.28 citric acid soda buffer solution. To this 0.25 cc 1 M-Na_2CO_3 is added. Distilled acetoaldehyde (0.5 cc) and deionized water (0.5 cc) are also added, and the tube is sealed. (When acetoaldehyde is added, there is some precipitation). This is allowed to react for 3 hours in a vessel having 50° C constant temperature. With a 6 N-HCl aqueous solution, the product is hydrolyzed for 12 hours under a reflux. The total is diluted to 50 cc, and a given amount of it is analyzed. The threonine standard material used is L-threonine. Quantitative analysis of the product is achieved by adding the standard material to the sample, and noting where the chromatogram peaks coincide.

In the case of reactions with acrylonitriles as well, the chains are dissolved in a pH 5.28 buffer solution. In one, Na_2CO_3 is added; the other is left unchanged. Acrylonitrile is added, and they are allowed to react.

Analysis of Sugars and Polyhydric Alcohols by Gas Chromatography /87

a) Preparation of the Column:

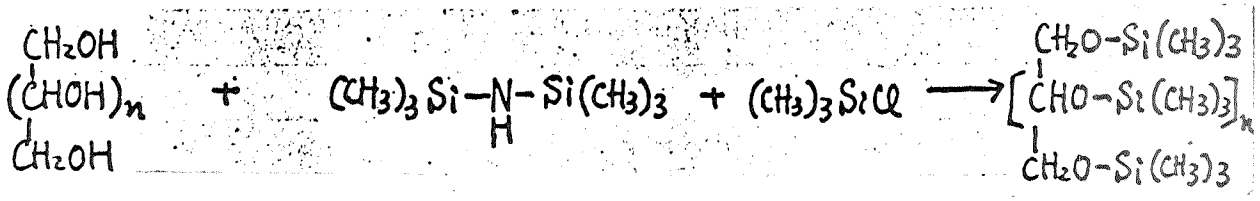
The fixed phase concentration was determined by the percentile weight of the fixed phase liquid with respect to the carrier (chromosorb W). PEG (polyethylene glycol) 1500, 4000, SE-30, HV silicone grease are measured out to give a specific weight percentage with respect to the carrier. The PEG is dissolved in methanol, the SE-30 in toluene, HV silicone grease in benzene and added to the carrier in the reaction vessel. The solvent is slightly more plentiful than the carrier. The reaction vessel is connected to a rotary evaporator and the solvent is evaporated by suction of a tap aspirator at a bath temperature of 60-70° C. It is then removed completely by a vacuum pump. It is put in a 3 m or a 1.8 m glass column and passed through nitrogen gas, the polyethylene glycol at 180° C, the SE-30 and HV silicone grease at 200-220° C. It is analyzed after overnight aging.

b) Carrier Processing by Trimethyl Chlorsilane:

The surface activity of chromosorb W is comparatively small, but in low liquid phase concentration analysis, tearing occurs due to adsorption of the sample. This was conspicuously present in the fixed phase of polyethylene glycol. To prevent this, the carrier fixed phase is treated with trimethyl chlorsilane before coating. A 5% (weight) toluene solution of trimethyl chlorsilane is prepared and added to the carrier in the reaction vessel, in quantities slightly greater than the carrier. This was placed in a reflux cooler, and steeped for 6-8 hours in a 60-70° C bath. It is filtered by a /88 glass filter, rinsed with methanol, and dried adequately with a vacuum pump.

c) TMS-ization of Sugars and Polyhydric Alcohols:

5 mg of the sample (sugar or polyhydric alcohol) is dissolved in 0.5 cc dry pyridine. When it is difficult to dissolve, as with L-sorbose, it is heated to 80° C. To this is added 0.1 cc hexamethyl disilazane and 0.05 cc trimethly chlorsilane. It is stoppered, and shaken well for 30 seconds. Large quantities of fine white precipitate are produced (assumed to be NH_4Cl). Since it does not hinder analysis, the white precipitate is not separated and 1-3 μl are taken in a microsyringe to charge the gas chromatograph. With respect to the dry pyridine, KOH grains are added over several days and the supernatant is used. The TMS-ized product thus obtained lasts from several hours to one day.



Polyhydric alcohol or sugar | Hexamethyl disilazane | Trimethyl chlorsilane | TMS-ized product

Hydrogen Peroxide Oxidation of Polyhydric Alcohols

a) Sorbitol Oxidation Reaction:

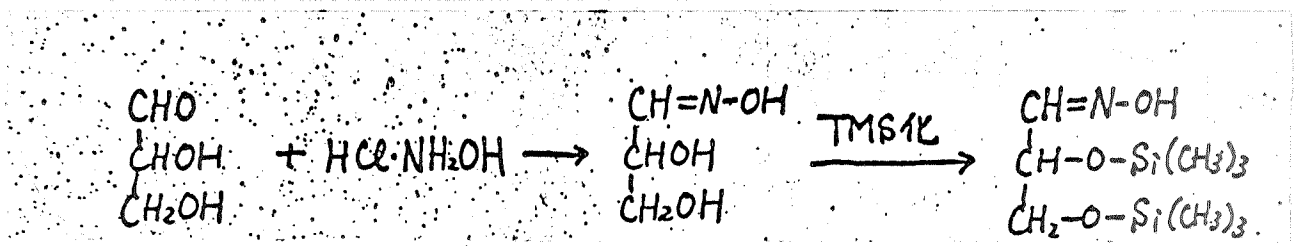
A 1-M sorbitol aqueous solution is prepared. 30% hydrogen peroxide is diluted with deionized water to give an approximately 1 M aqueous solution. A 0.1 M aqueous solution of $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $Cu(AAN)_2SO_4$, $Cu(NH_2CH_2\overset{O}{\overset{\|}{C}}{=}NH)_2 \cdot H_2O$ is prepared. 5 cc sorbitol solution and 2 cc catalyst /89 solution are mixed. 5 cc hydrogen peroxide solution is added, and it is allowed to react at room temperature. In the case of both $FeSO_4$ and $CuSO_4$ catalysts, there was no gas generated and no precipitate produced. However,

when a $Cu(NH_2CH_2\overset{\rho}{C}=NH)_2$ catalyst was used, as soon as the H_2O_2 was added, there was immediate gas generation, and a dark green precipitate was produced. In the case of the $Cu(AAN)_2SO_4$ catalyst, when the H_2O_2 was added, a black-brown precipitate was produced followed after some time by gas generation. After several days, the black-brown precipitate was dissolved again. The gas was assumed to be oxygen. These reaction liquids were kept for a while, and then 5 cc of each was taken and H_2S was used to precipitate out all the metal sulfates. The filtrate was diluted to 10 cc. 1 cc was placed in a vessel, attached to a rotary evaporator, and the water component was completely removed by vacuum pump suction at a bath temperature of 60° C. 1 cc dried pyridine is added to the residue, and the product is dissolved in pyridine at an 80° C bath temperature. It was TMS-ized by adding hexamethyl disilazane and trimethyl chlorsilane and 2 μl was used to charge the gas chromatograph.

b) Glycerine Oxidation Reaction:

In the case of a $FeSO_4$ catalyst, equal amounts are removed by a pipette from 1 M-$FeSO_4$ solution, 5 M-H_2O_2 solution, and 3 M-glycerine solution to prepare a reaction liquid. In the case of a $CuSO_4$ catalyst, equal amounts are taken from a 1 M-$CuSO_4$ solution, 1 M-H_2O_2 solution, and 1 M-glycerine /90
solution to prepare the reaction liquids. In the case of a $Cu(AAN)_2SO_4$ catalyst, equal amounts are removed from 0.5 M-$Cu(AAN)_2SO_4$ solution, 5 M-H_2O_2 solution, and 3 M-glycerine solution by pipette to prepare the reaction liquids. The reaction liquids described above are allowed to react in a bath temperature of 50° C.

A given amount of reaction liquid is measured out by pipette, and after metallic ions are removed in the form of sulfates, it is condensed and in a pyridine solution, an excess of hydroxyl amine chloride is added. It is heated at 80° C for 1-2 hours for oximization, dried, dissolved in pyridine, and changed to trimethyl silyl ether. 1-2 μl is used to charge the gas chromatograph.



Glycerine aldehyde

Glycerine aldehyde oxime

CONCLUSION

We are grateful to Professor Shiro Morimoto and Professor Seiichi Kanda for the guidance in the preparation of this paper. We are also thankful to Mr. Hidefumi Yoshida for his help in amino acid analysis.

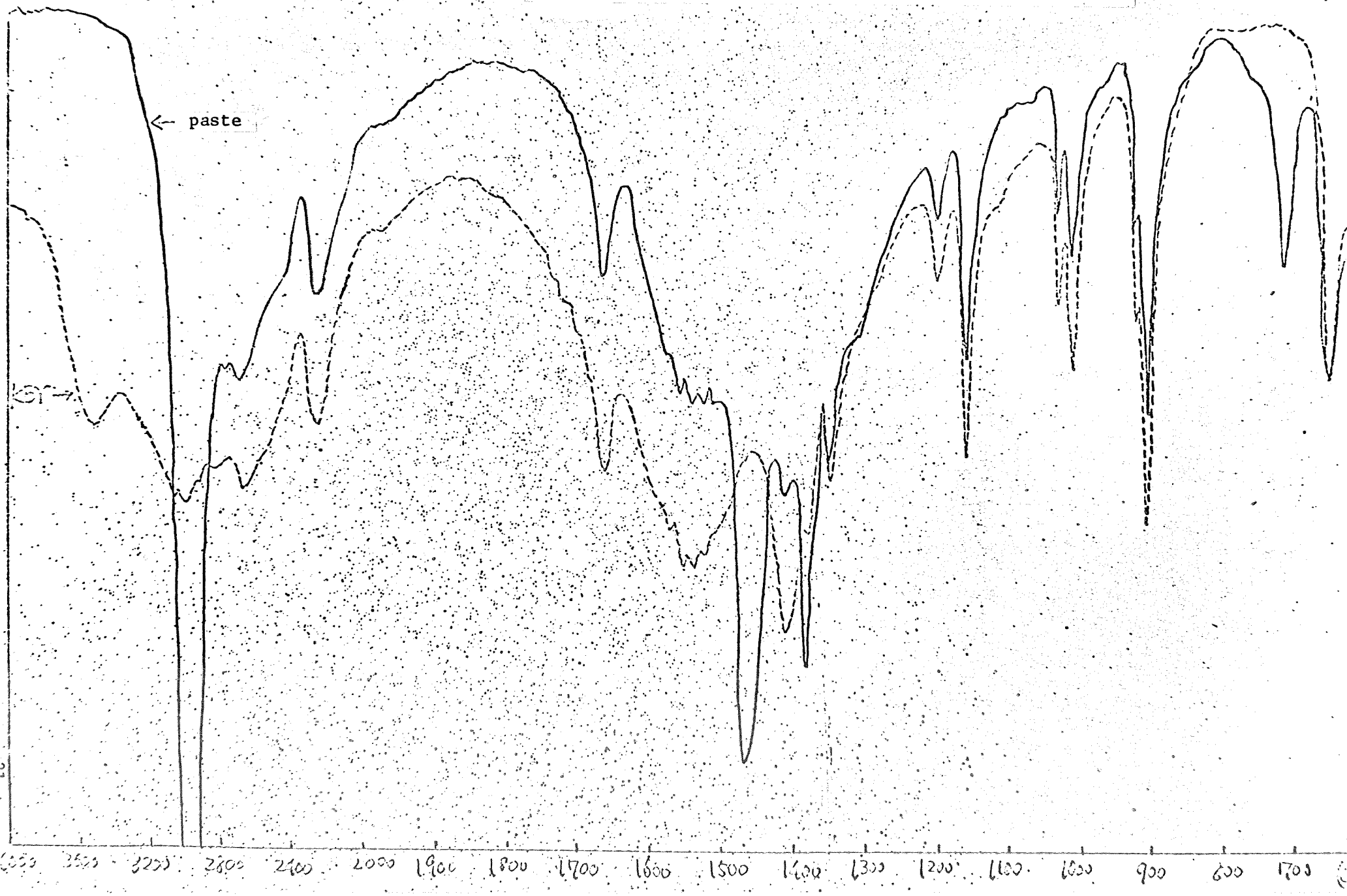
TABLE 1. PRODUCTS OF REACTION OF $CuSO_4 \cdot 5H_2O$ AND AMINOACETONITRILE ACETATE (WATER-EtOH GROUP).

Exp. No.	Reagent			Element Analysis Value					Yield	Color
	$CuSO_4 \cdot 5H_2O$ mol/cc	AAN·AcOH mol/cc	Cu/AAN	H %	C %	N %	Cu[a] %	Cu[b] %	g	
1	0.01/50	0.005/50	1:0.5	2.52	4.04	4.59	27.49	35.36	0.2086	pale blue
2	0.005/25	0.005/25	1:1	2.34	6.34	7.32	25.29	34.08	0.5793	"
3	0.005/25	0.0067/25	1:1.34	2.51	8.33	9.54	22.28	32.41	0.5868	"
4	0.01/50	0.015/50	1:1.5	2.50	11.54	13.33	21.97	29.73	1.1726	"
5	0.01/50	0.02/50	1:2	2.90	16.67	19.13	24.49	23.72	2.3232	blue
6	0.01/50	0.04/50	1:4	2.66	17.75	20.58	22.99	22.65	2.4740	"
7	0.01/50	0.08/50	1:8	2.88	17.50	19.99	23.42	23.00	2.2376	pale blue

TABLE 1-b. THEORETICAL VALUES FOR ELEMENT ANALYSIS OF Cu-AAN CHAINS

Cu-AAN chains	Cu	C	H	N	SO_4	O
$Cu(AAN)_2SO_4$	23.38	17.68	2.97	20.61	35.35	
$Cu(AAN)SO_4$	29.46	11.14	1.87	12.99	44.54	
$Cu(AAN)SO_4 \cdot H_2O$	27.19	10.27	2.59	11.99	41.11	
$Cu(AAN)SO_4 \cdot 2H_2O$	25.25	9.54	2.20	11.13	38.16	
$Cu(AAN)_4SO_4$	16.55	25.03	4.20	29.20	25.02	
$Cu(AAN)_3SO_4 \cdot H_2O$	18.38	20.83	4.86	24.30	27.78	4.63
$Cu(AAN)_2SO_4 \cdot H_2O$	21.93	16.58	3.48	19.34	33.15	5.52
$Cu(AAN)_2SO_4 \cdot 2H_2O$	20.65	15.61	3.93	18.20	31.21	10.40
$Cu(AAN)_2SO_4 \cdot \frac{1}{2}H_2O$	22.63	17.11	3.23	19.96	34.22	2.85
$Cu(AAN)_3SO_4$	19.38	21.98	3.69	25.64	29.30	

Figure 1-1. Infrared absorption spectrum for AAN-AcOH.



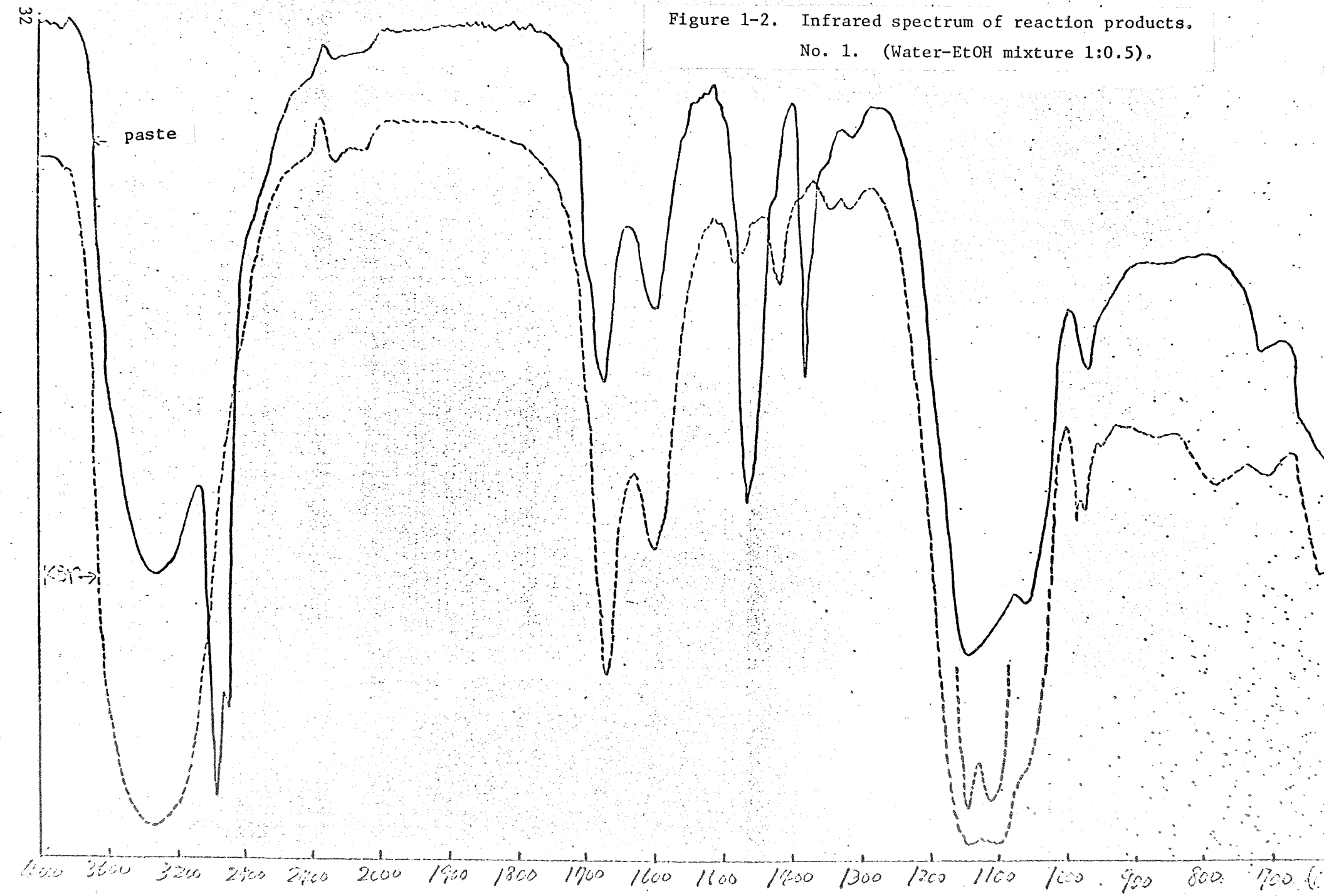
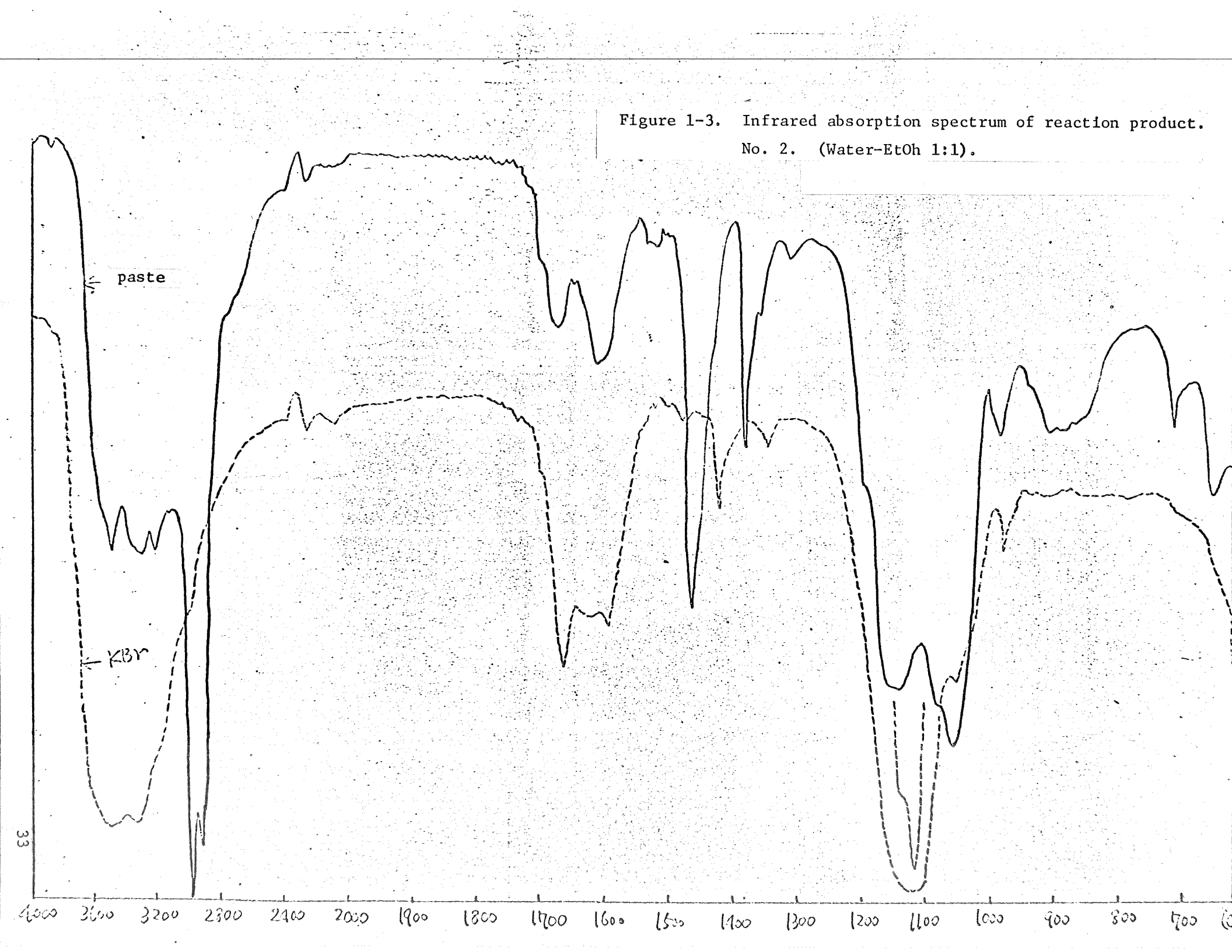


Figure 1-2. Infrared spectrum of reaction products. No. 1. (Water-EtOH mixture 1:0.5).

Figure 1-3. Infrared absorption spectrum of reaction product. No. 2. (Water-EtOh 1:1).



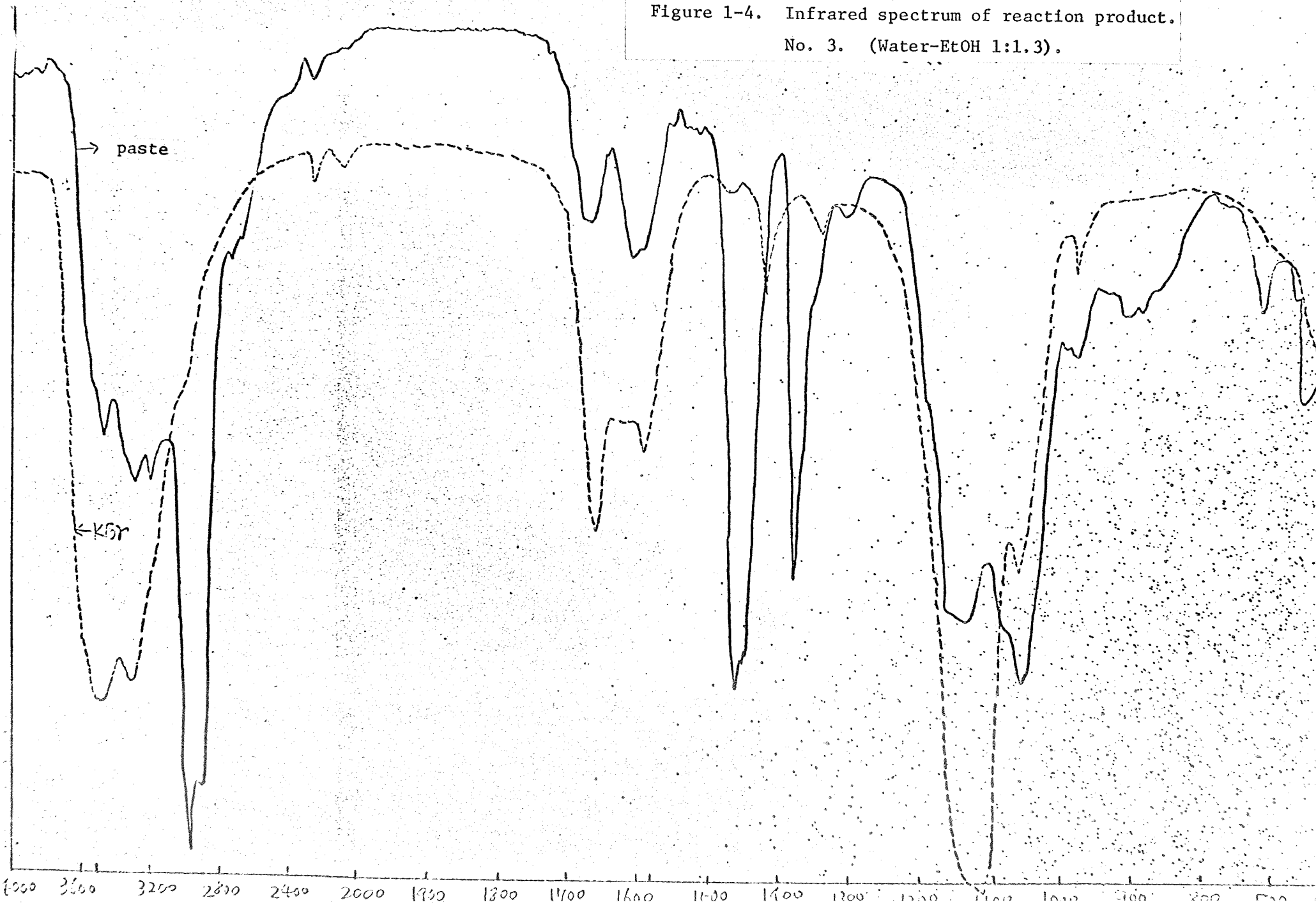


Figure 1-4. Infrared spectrum of reaction product. No. 3. (Water-EtOH 1:1.3).

Figure 1-5. Infrared absorption spectrum.
No. 4. (Water-EtOH 1:1.5).

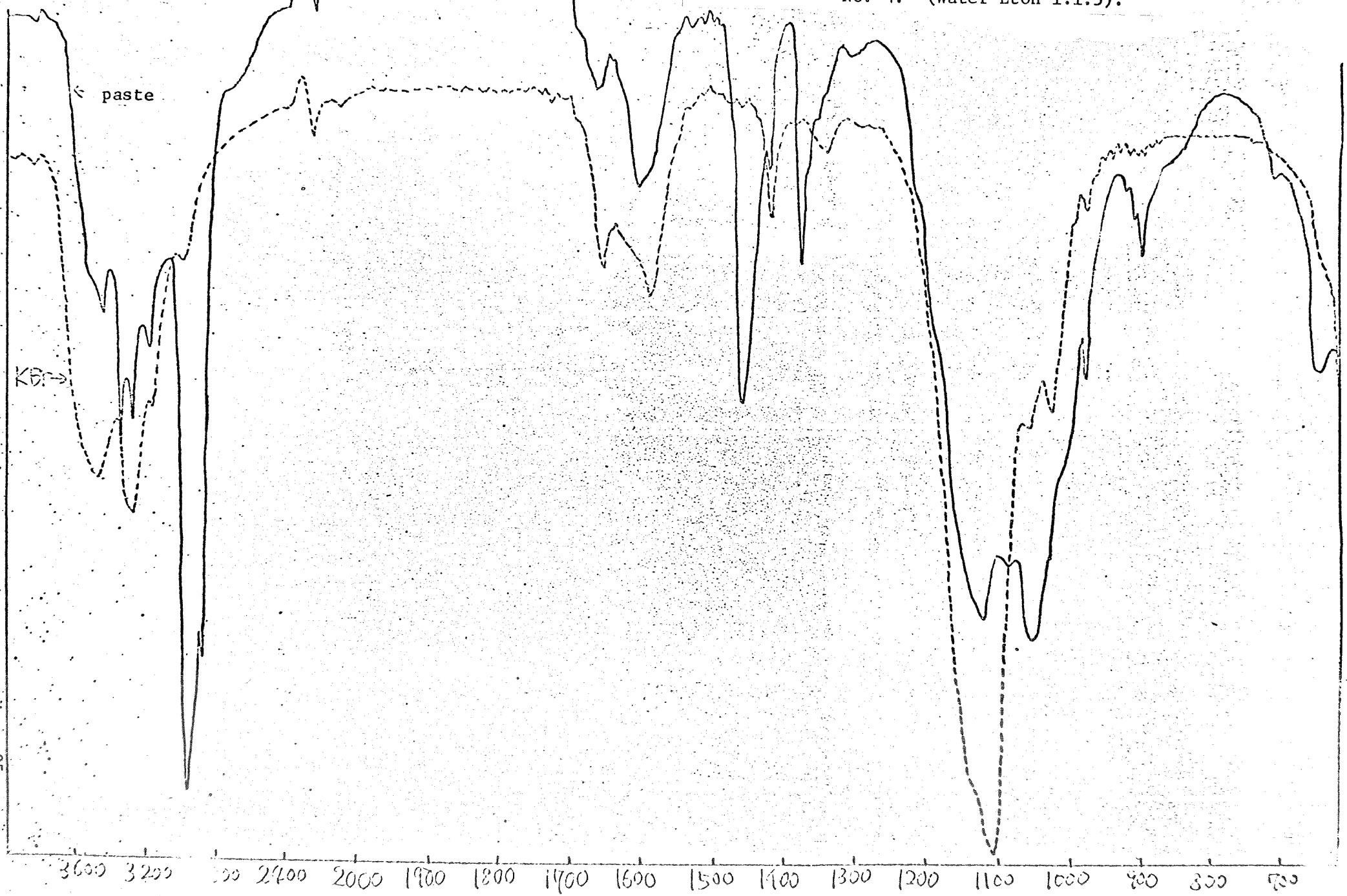


Figure 1-6. Infrared absorption spectrum of reaction product. No. 5. (Water-EtOH 1:2).

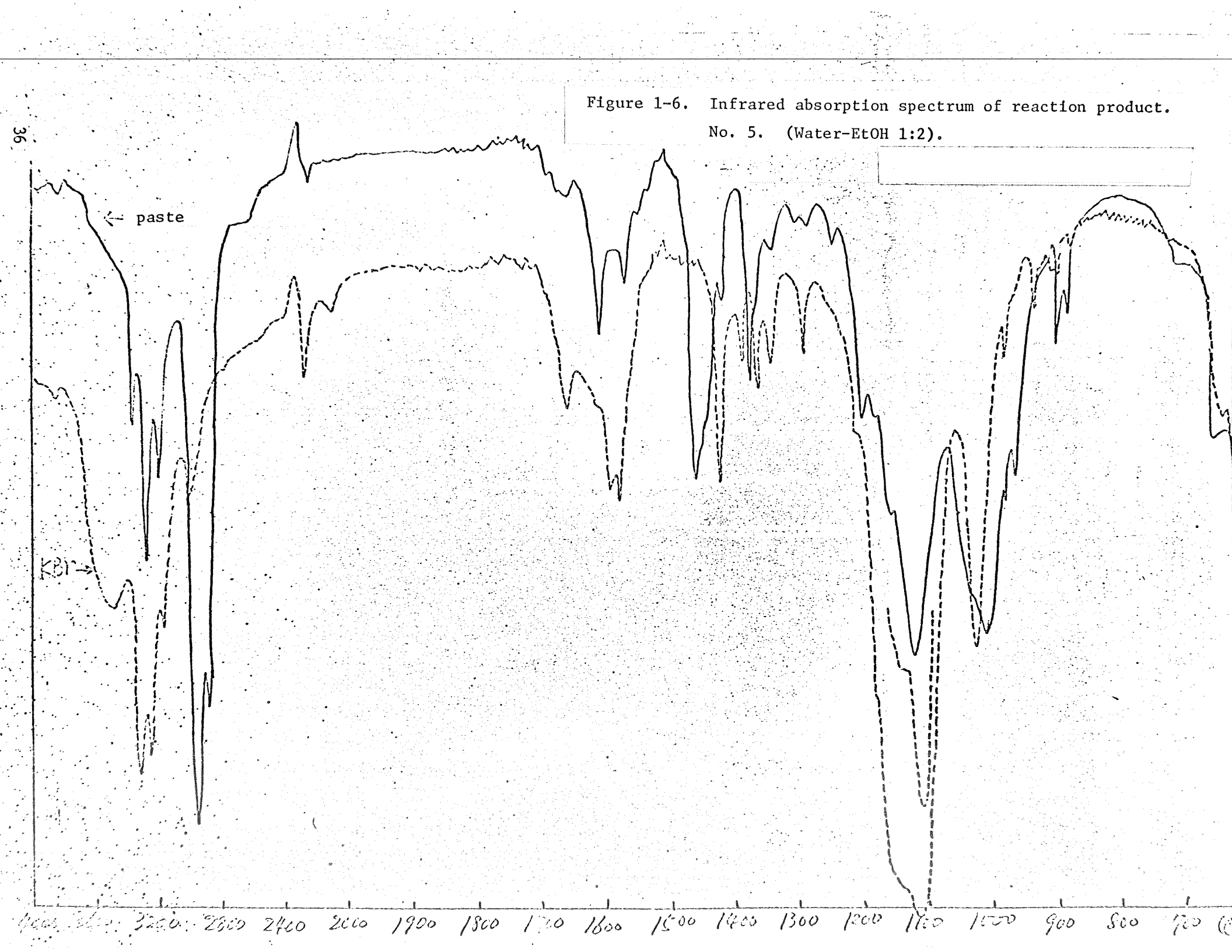


Figure 1-7. Infrared absorption spectrum of reaction product. No. 6. (Water-EtOH 1:4).

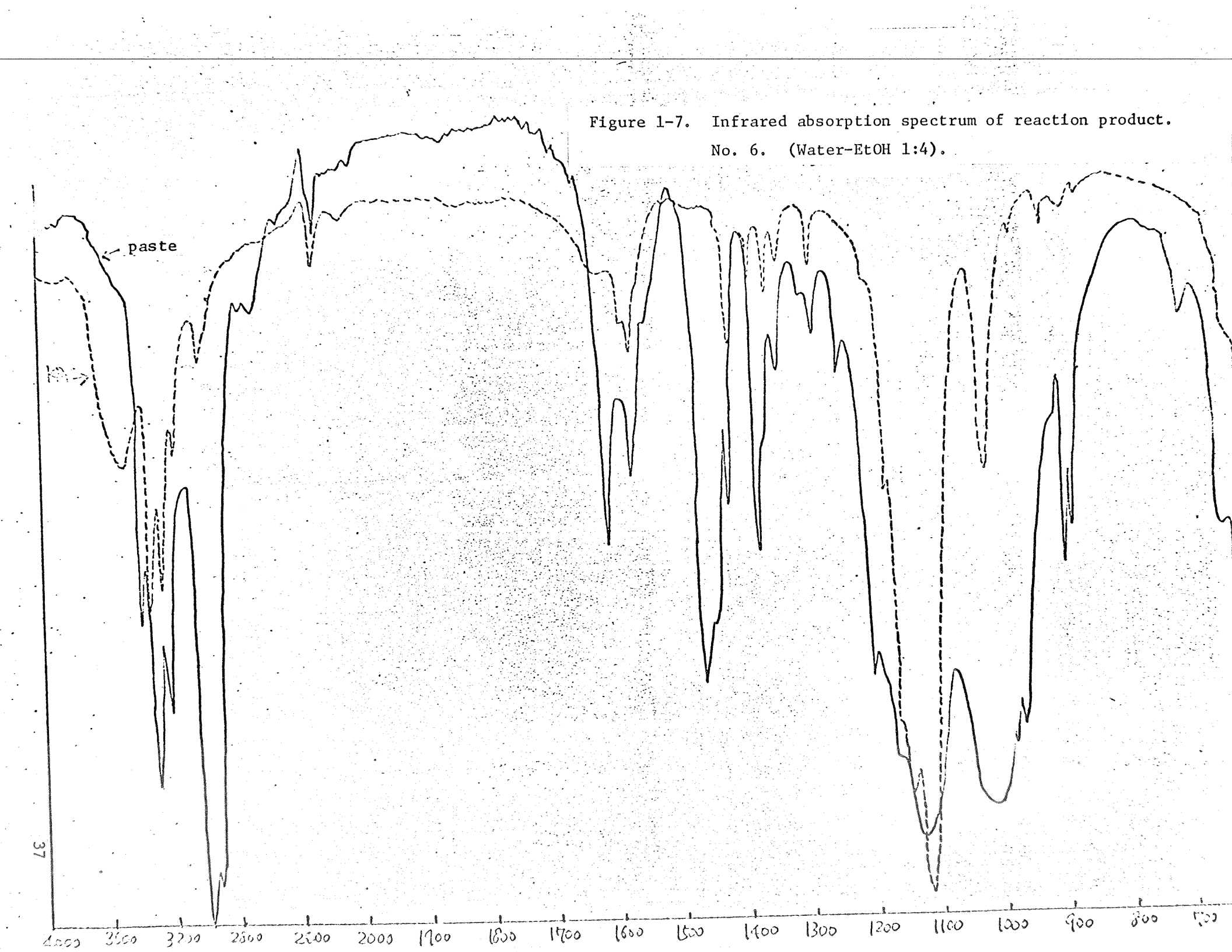


Figure 1-8. Infrared absorption spectrum of reaction product. No. 6. (Water-EtOH 1:8).

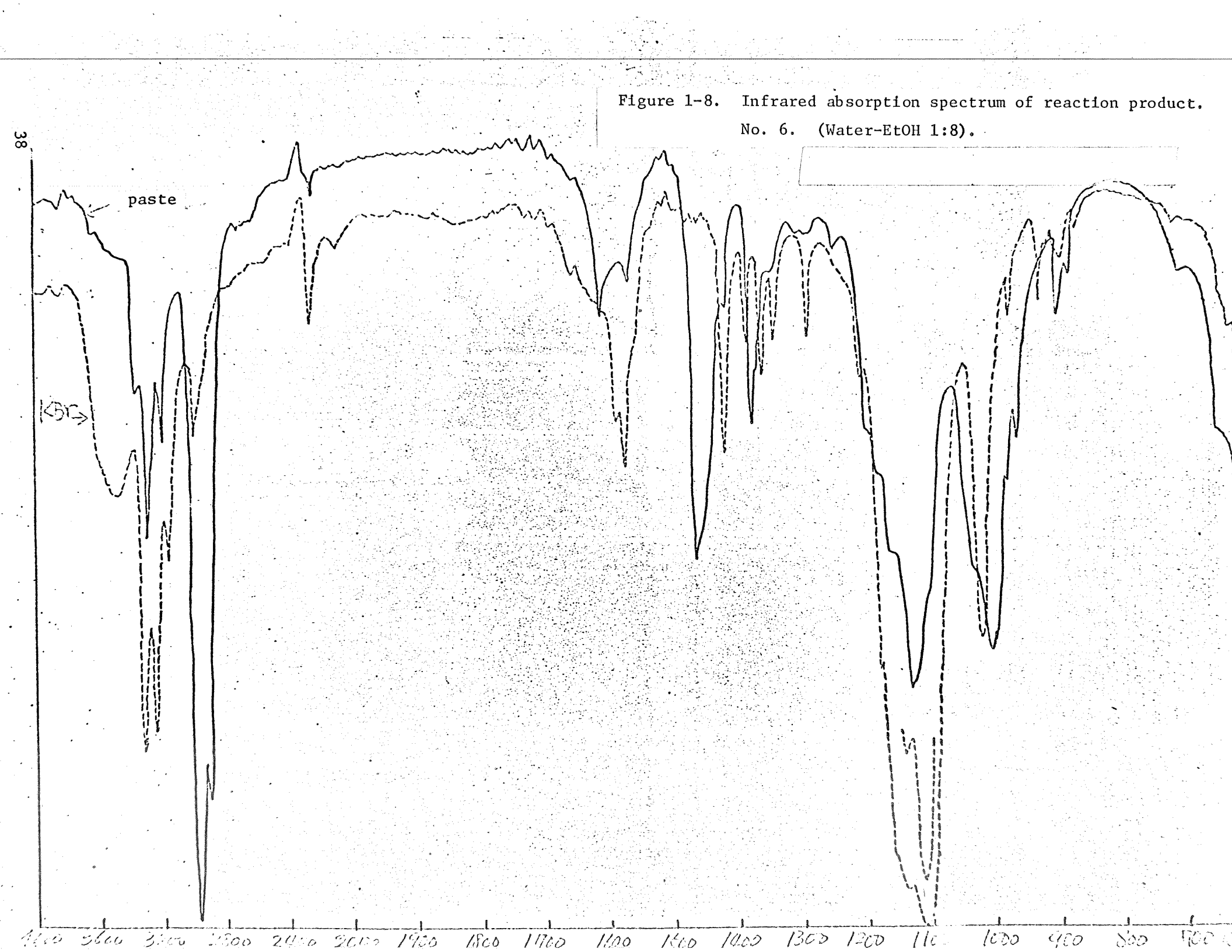
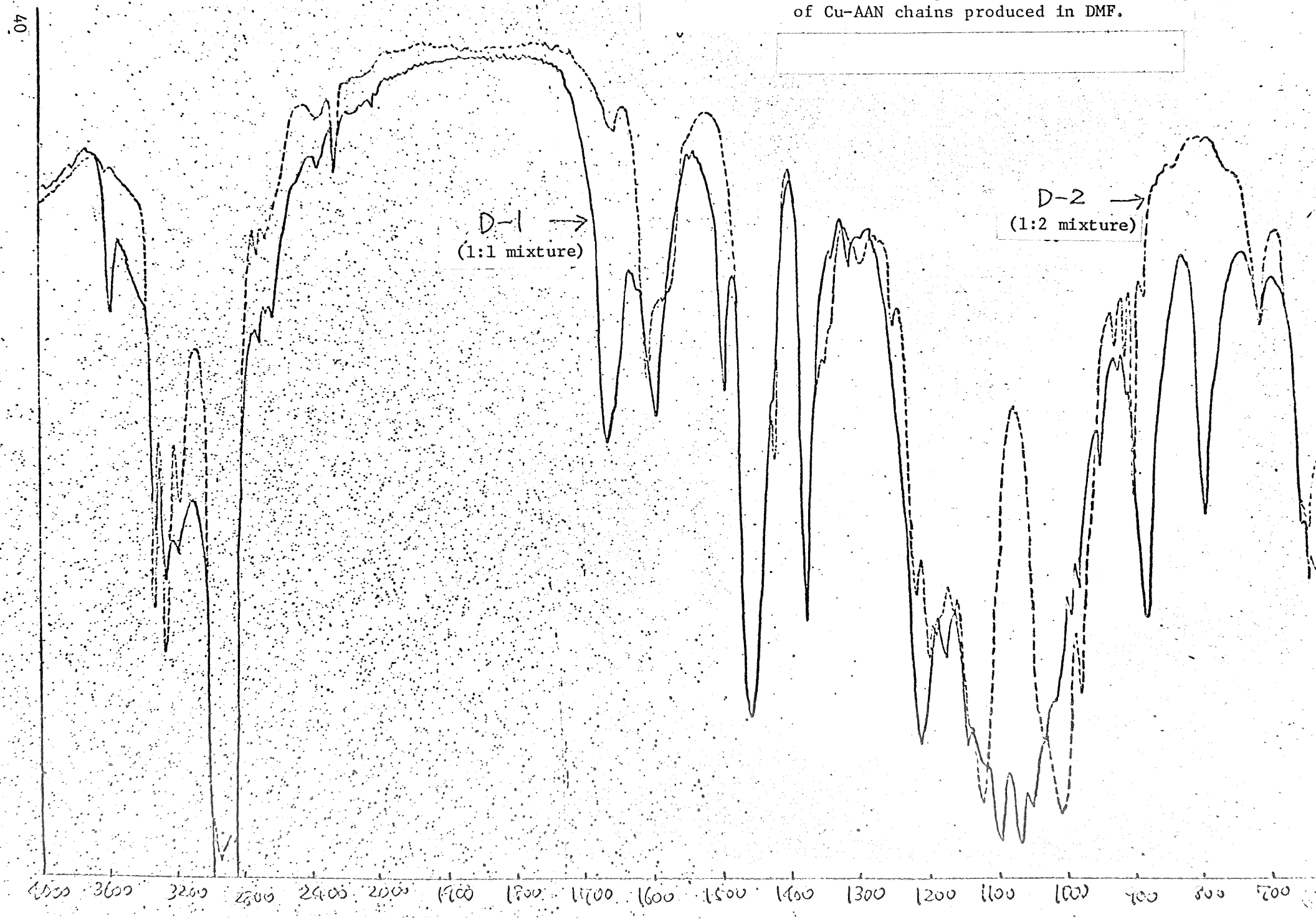


TABLE 2. PRODUCTS OF REACTION OF AMINOACETONITRILE ACETATE AND $CuSO_4 \cdot 5H_2O$ IN DMF.

Exp. No.	Reagent			Element Analysis Value					Yield	Color
	$CuSO_4 \cdot 5H_2O$ mol/cc	AAN/AcOH mol/cc	Cu/AAN	H %	C %	N %	Cu^a %	Cu^b %	gr.	
D-1	0.005/20	0.005/10	1:1	2.75	12.68	13.80	27.52	25.55	0.5382	blue
D-2	0.005/25	0.01/20	1:2	2.77	17.34	20.17	23.21	23.86	1.2173	"
D-3	0.005/20	0.02/15	1:4	2.89	17.78	20.94	22.04	23.01	1.2875	"
D-4	0.0025/15	0.02/20	1:8	2.97	17.29	20.27	20.09	21.85	0.5920	"

Figure 2-1. Infrared absorption spectrum (paste) of Cu-AAN chains produced in DMF.



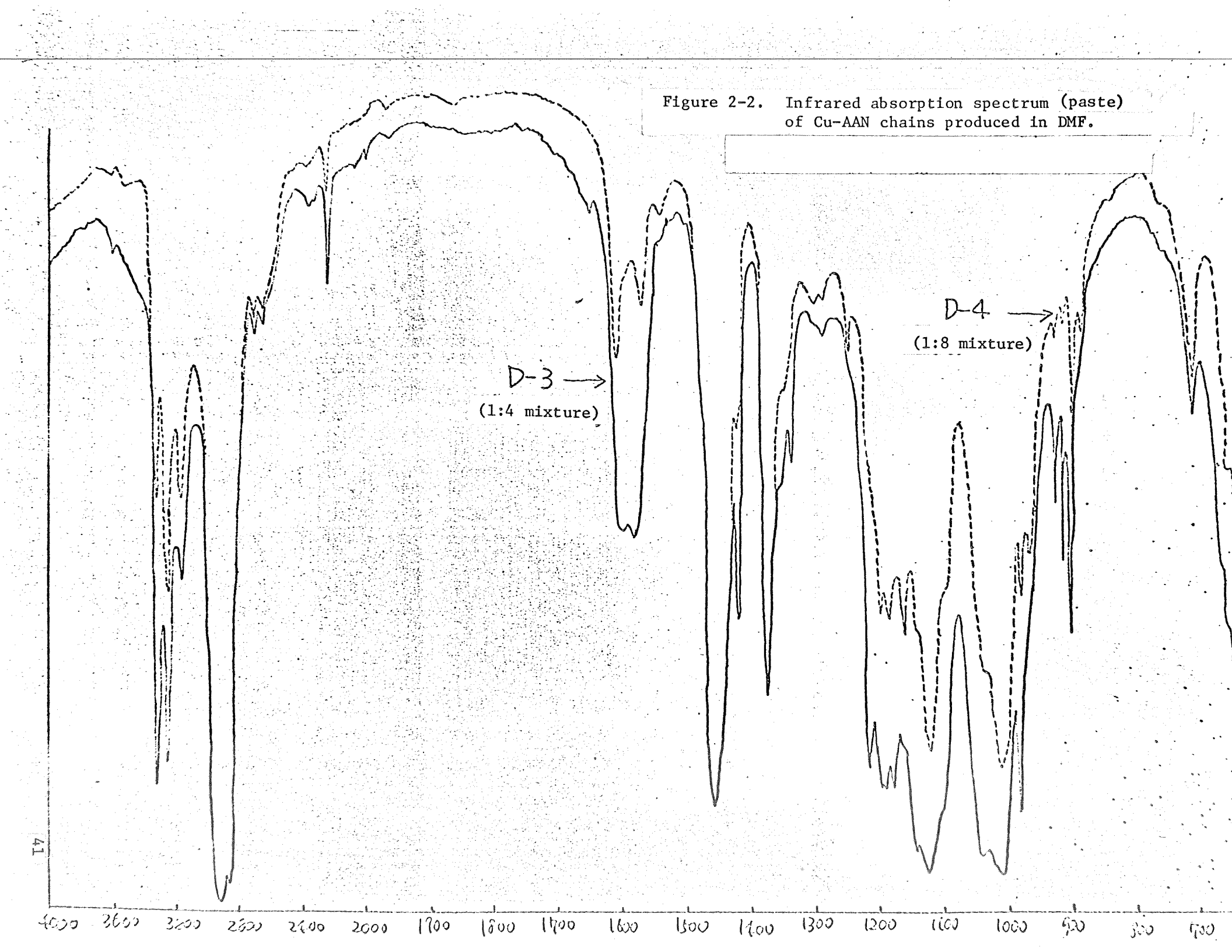


Figure 2-2. Infrared absorption spectrum (paste) of Cu-AAN chains produced in DMF.

TABLE 3. PRODUCTS OF REACTION OF AMINOACETONITRILE ACETATE AND $CuSO_4 \cdot 5H_2O$ IN METHANOL.

Exp. No.	Reagent			Element Analysis Value					Yield	Color
	$CuSO_4 \cdot 5H_2O$ mole/cc	AAN·AcOH mole/cc	Cu/AAN	H %	C %	N %	Cu[a] %	Cu[b] %	gr	
M-1	0.005/20	0.005/10	1:1	2.69	12.84	13.38	(39.95)	25.69	0.3756	pale blue
M-2	0.005/20	0.01/10	1:2	3.06	16.12	20.05	22.14	2.83	1.2186	"
M-3	0.005/20	0.02/10	1:4	3.24	18.67	21.99	23.76	20.73	1.1957	"
M-4	0.0025/10	0.02/10	1:8	3.43	19.42	22.71	12.79	13.64	0.5203	blue
M-5	0.0025/10	0.025/10	1:10	3.59	20.00	23.33	13.96	15.07	0.5216	blue gray

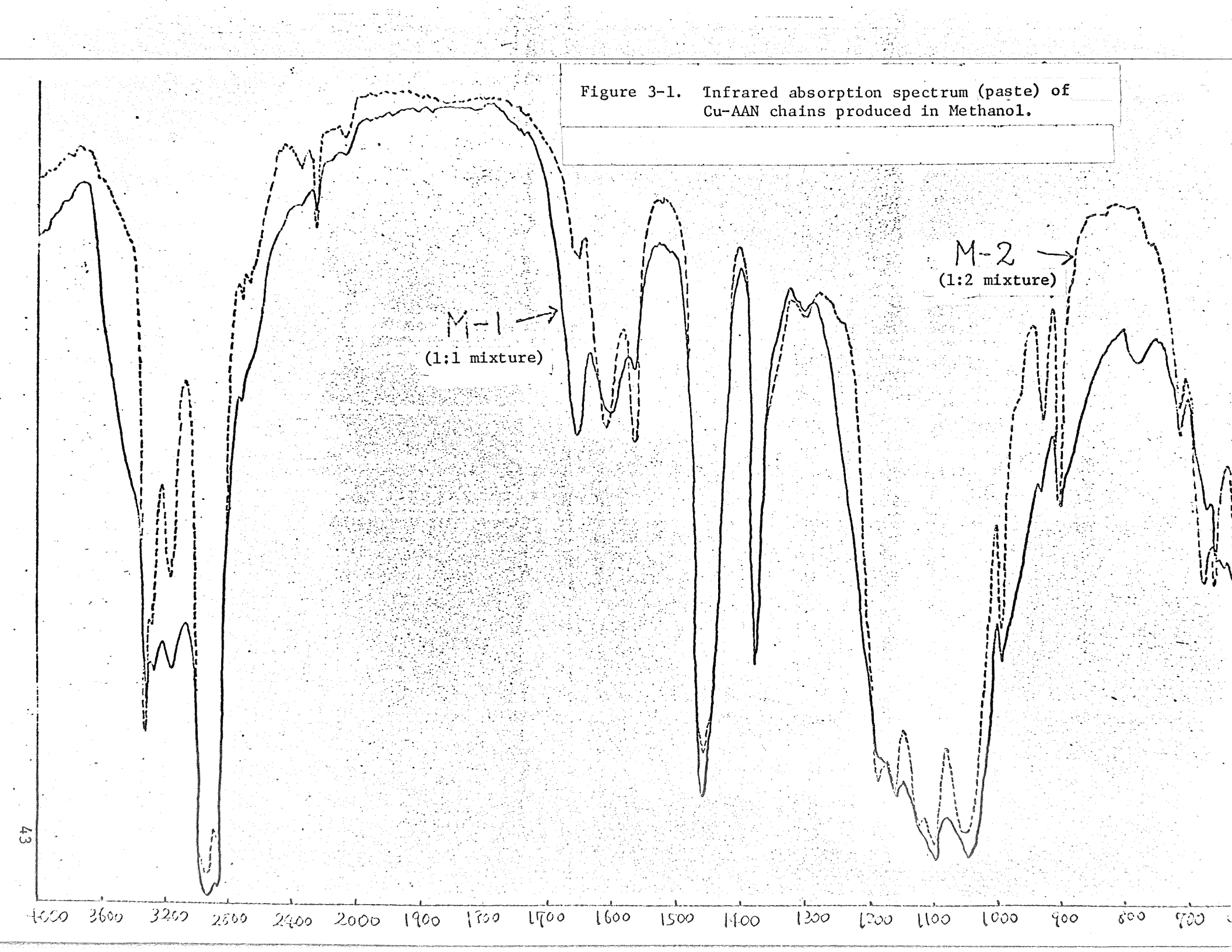


Figure 3-1. Infrared absorption spectrum (paste) of Cu-AAN chains produced in Methanol.

Figure 3-2. Infrared absorption spectrum (paste) of Cu-AAN chains produced in Methanol.

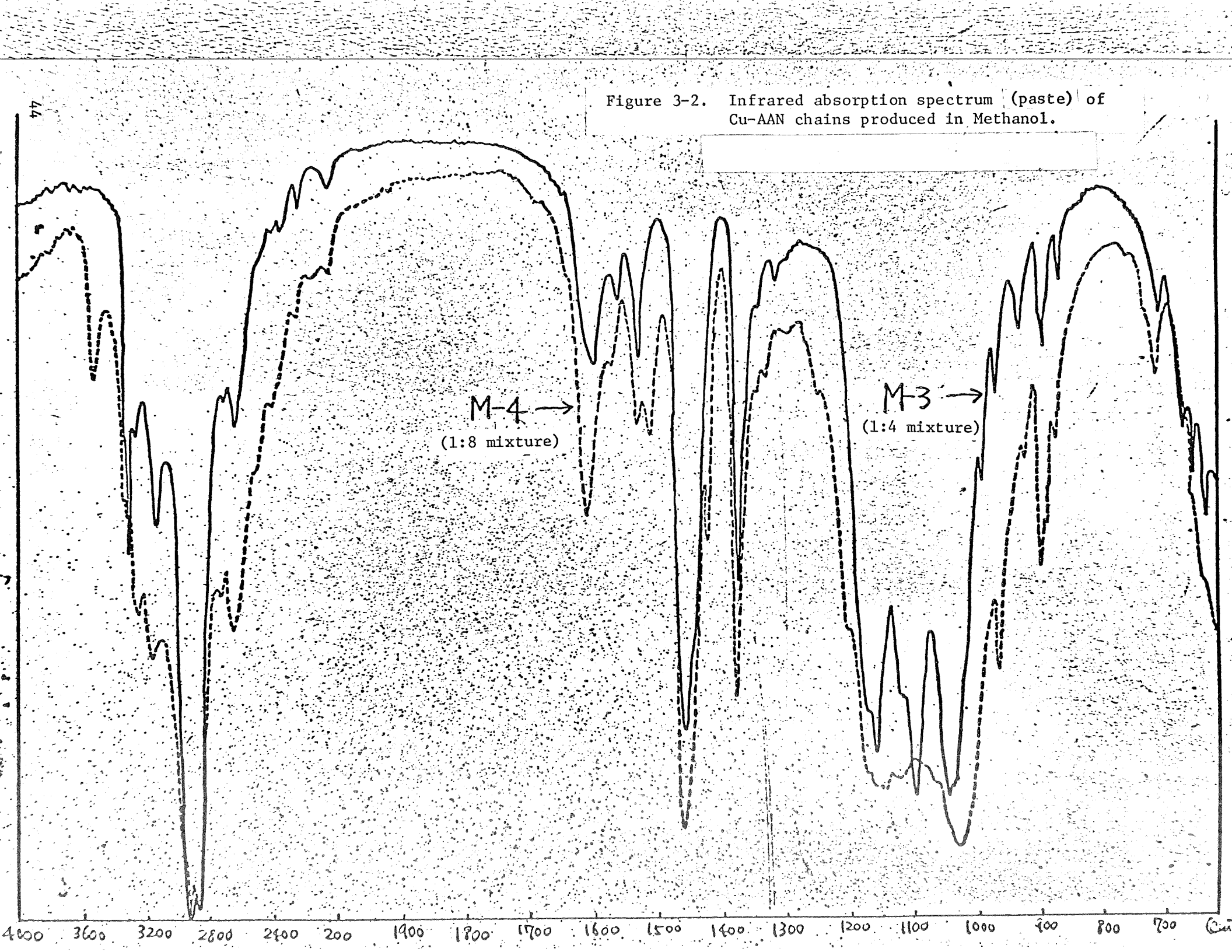


TABLE 4-a. INFRARED ABSORPTION SPECTRUM OF AAN-AcOH AND REACTION PRODUCT.

(paste) (1)

Wave No.	AAN-AcOH	No.1 (1:2.5)	No.2 (1:1)	No.3 (1:1.3)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:6)
3470	——		Sh	Sh	Sh			
3430	——		++	++	++			
3330	——		3310(Sh)	3310(Sh)	++	++	++	+
3250	——	+++	+	+	++	+++	+++	+++
3160			+	+	+	++	+++	+++
2700	+		Sh	+		+	+	+
2590	2630(+)				Sh	+	+	+
2250	+		+	+	+	+	+	+
1680	1670(Sh)	Sh	Sh	Sh	Sh	Sh	Sh	Sh
1655	——	1660(+)	++	++	1653(+)			
1652	++							
1650	——					+		
1600		1595(+)	++	++	1595(++)	++	1603(+)	++
1568	——			1570(Sh)	1570(Sh)	1563(+)	++	1560(+)
1545	+	1550(Sh)			+			
1550			Sh	Sh				
1540	+							

(continued)

TABLE 4-a. INFRARED ABSORPTION SPECTRUM OF AAN-AcOH AND REACTION PRODUCT (continued).

(paste)

Wave No.	AAN-AcOH	No.1 (1:0.5)	No.2 (1:1)	No.3 (1:1.3)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:7)
1520	+							
1420		1423(Sh)	Sh	Sh	+	+	++	++
1410	+							
1355	+				Sh			
1342		1350(Sh)	Sh	1350(Sh)	Sh	+	+	+
1310	Sh	1315(Sh)	+	+	+	+	+	1315(+)
1295				Sh		1293 (+)		
1266						+	+	+
1207						++	+	Sh
1205	++		Sh					
1194			Sh	Sh	Sh			
1174				Sh	1154(Sh)	1156 (+)	Sh	1150(Sh)
1160							Sh	
1140	++		Sh			Sh		Sh
1100		++		++	Sh			
1037					1020(+)	1026(+)	+++	+++
1064			Sh	Sh	+++			

(continued)

TABLE 4-a. INFRARED ABSORPTION SPECTRUM OF AAN-AcOH AND REACTION PRODUCT (continued).

(paste)

Wave No.	AAN-AcOH	No.1 (1:3)	No.2 (1:1)	No.3	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:8)
1037	+	1038(++)	1038(++)	1040(+++)				
1028	+++					+	+++	
1011					+++	+++		1010(+++)
990			+	+	+	+	++	+
972		970(+)				967(+)		967(+)
937					930 (+) sh (-)	sh	sh	
912	++							
907			+	+	++	++	++	++
873			887(+)	+		+	++	+

sh: type

+<++<+++

(concluded)

TABLE 4-b. INFRARED ABSORPTION SPECTRUM OF AAN-AcOH AND REACTION PRODUCT

KBr

Wave No.	AAN-AcOH	No.1 (1:3.5)	No.2 (1:1)	No.3 (1:1.3)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:2.9)	No.7 (1:5)
3450	+		+++	+++	++	++	++	++
3260		+++	Sh	Sh	++	++	++	++
3140						+	++	++
3120					3150 Sh	+	+	+
2960		Sh	Sh	+	+	+	+	+
2940	+							
2860	+							
2400	+							
2250	++			+	+	+	+	+
2090				+	+	+	+	+
1650		++						
1650			++	++	++			
1620			+	+				
1610							+	+
1587		++	++					
1550				1520 Sh	++	++	++	++

(continued)

TABLE 4-b. INFRARED ABSORPTION SPECTRUM OF AAN-AcOH AND REACTION PRODUCT (continued)

KBr

Wave No.	AAN-AcOH	No.1 (100.5)	No.2 (4.1)	No.3 (1:6.2)	No.4 (1:2.5)	No.5 (1:2)	No.6 (1:1)	No.7 (1:0.5)
1567						+	+	+
1565					sh	sh	sh	sh
1420	sh	+	+	+	+	+	++	++
1410	+							
1385						+	+	+
1370	sh		+					
1360						+	+	+
1350	+							
1340			1342(sh)	1342(sh)	+	1342(+)	+	+
1310		+						
1295						+		+
1275						sh	+	+
1205	+							
1164					sh	sh	sh	+
1144	++				sh	sh	+	+

(continued)

TABLE 4-b. INFRARED ABSORPTION SPECTRUM OF AAN-AcOH AND REACTION PRODUCT (continued)

KBr

Wave No.	AAN-AcOH	No.1 (30.0)	No.2 (4.1)	No.3 (3.6)	No.4 (1.6)	No.5 (1.2)	No.6 (1.5)	No.7 (1.8)
1146							++	+
1104		+++	Sh	+++	Sh		+	+
1122			+++					
1114						+++	+++	+++
1042	+							
1029					+	++	++	++
1017	+							
1059	+		+	+				
987		+	+	+	+	+	+	+
924								
927	+	950(+)				+	+	+
917	++							
707					+	+	+	+

Sh type

+<++<+++

Figure 4-1. Powder X-ray analysis pattern.
Experiment No. 2 (1:1 Water-EtOH mixture).

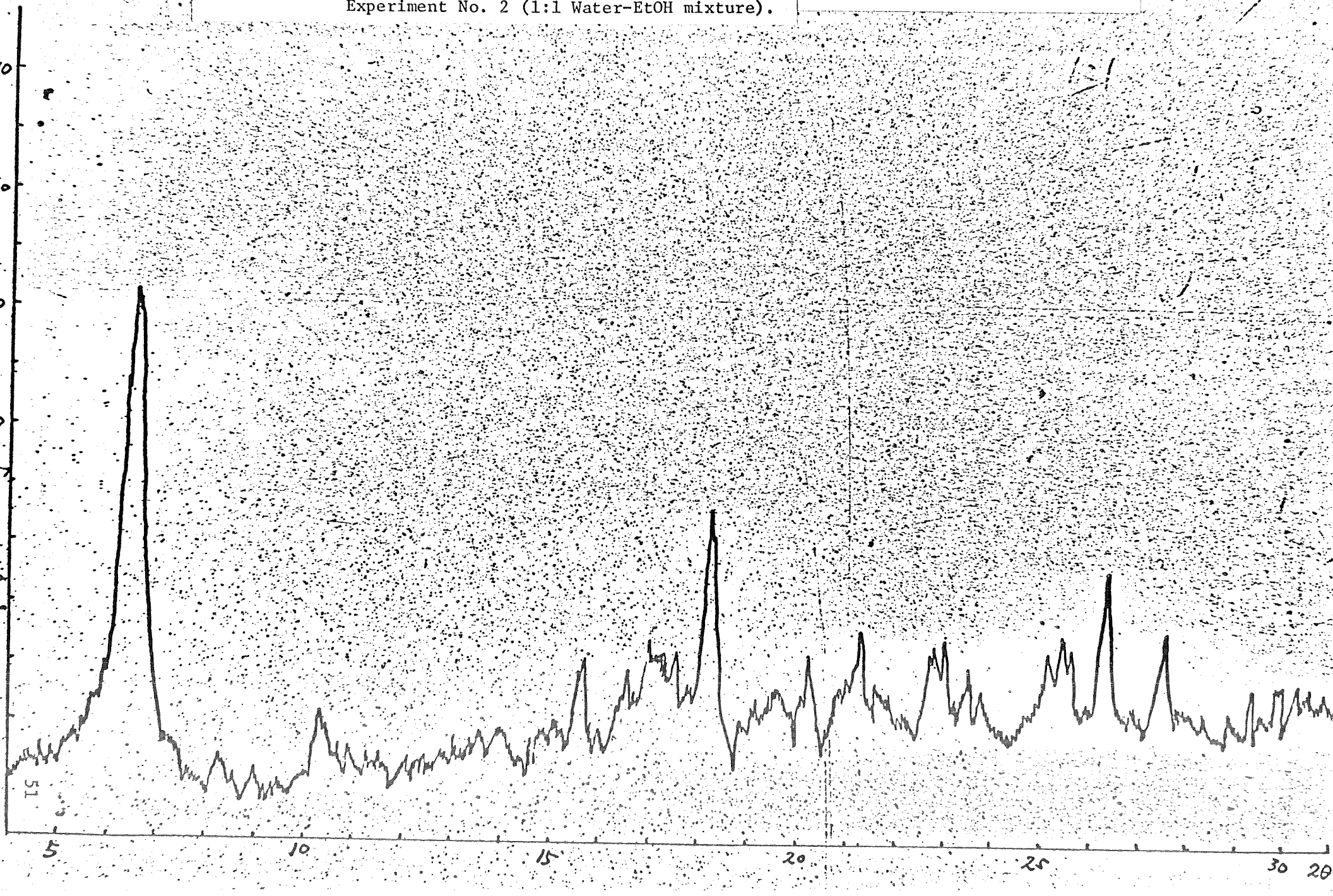


Figure 4-2. Powder X-ray analysis pattern.
Experiment No. 4 (1:1.5 water EtOH mixture).

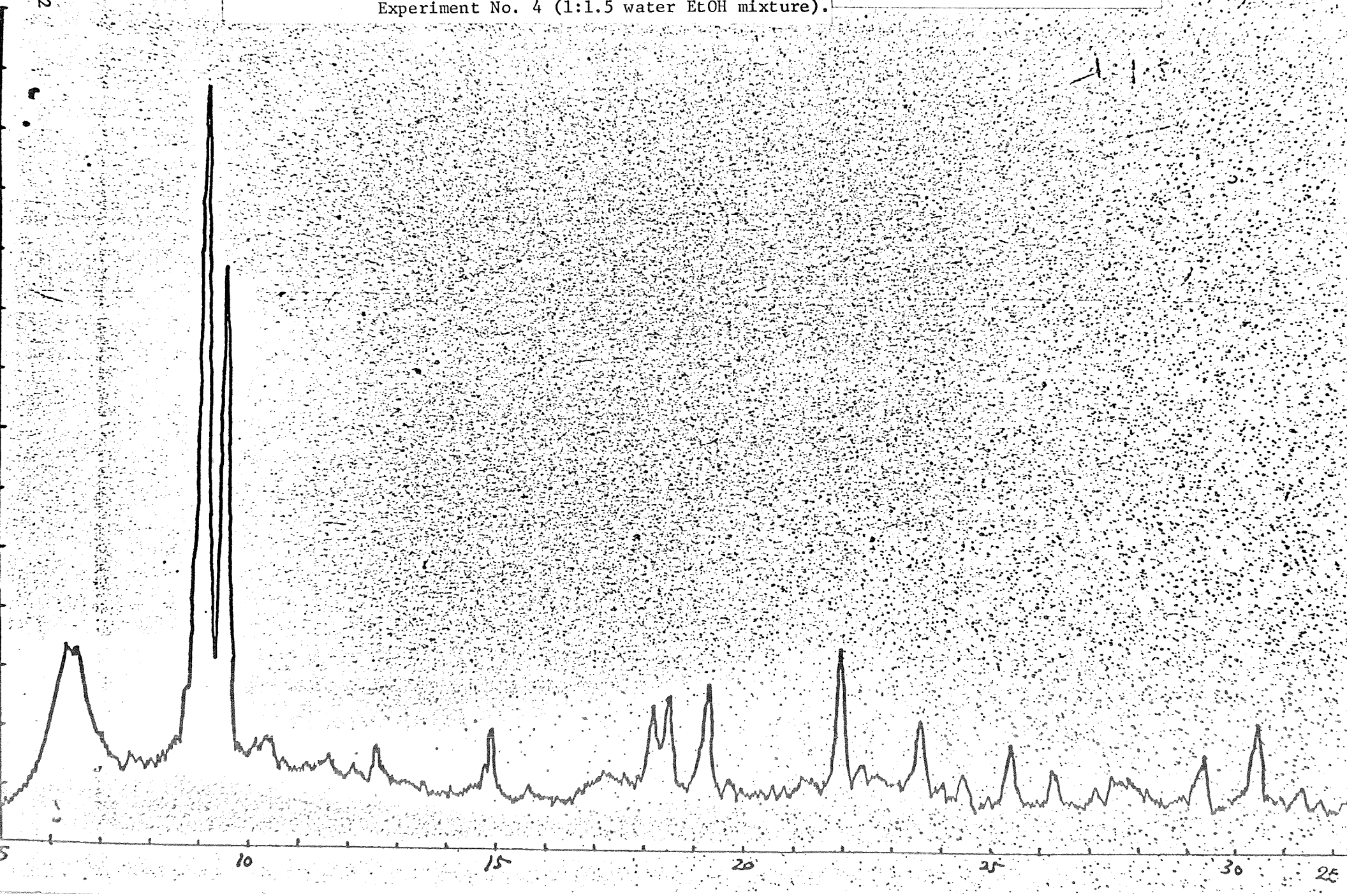


Figure 4-3. Powder X-ray analysis pattern.
Experiment No. 5 (1:2 Water-EtOH mixture).

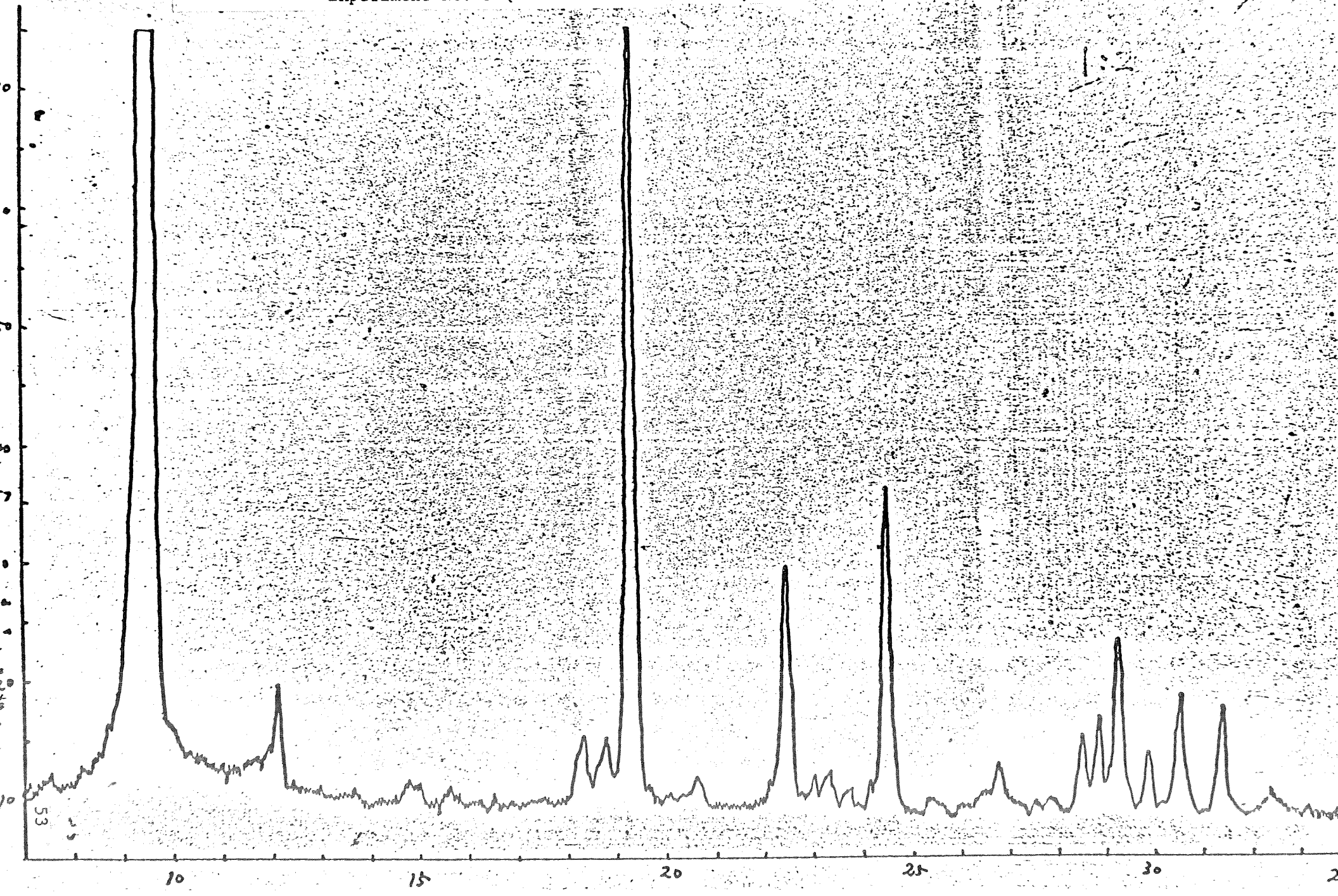


Figure 4-4. Powder X-ray analysis pattern.
Experiment No. 6 (1:4 Water-EtOH mixture).

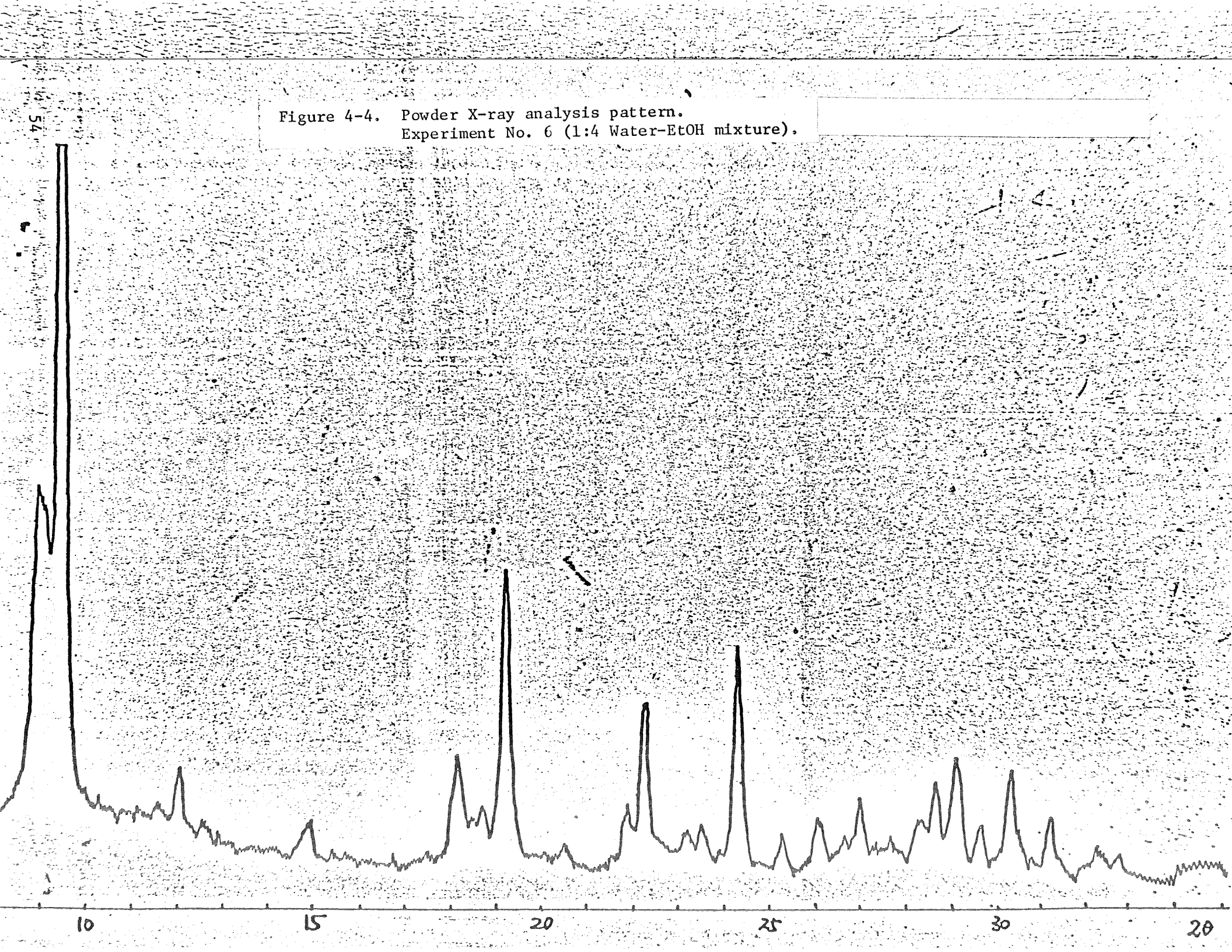


Figure 4-5. Powder X-ray analysis pattern.
Experiment No. 7 (1:8 Water-EtOH mixture).

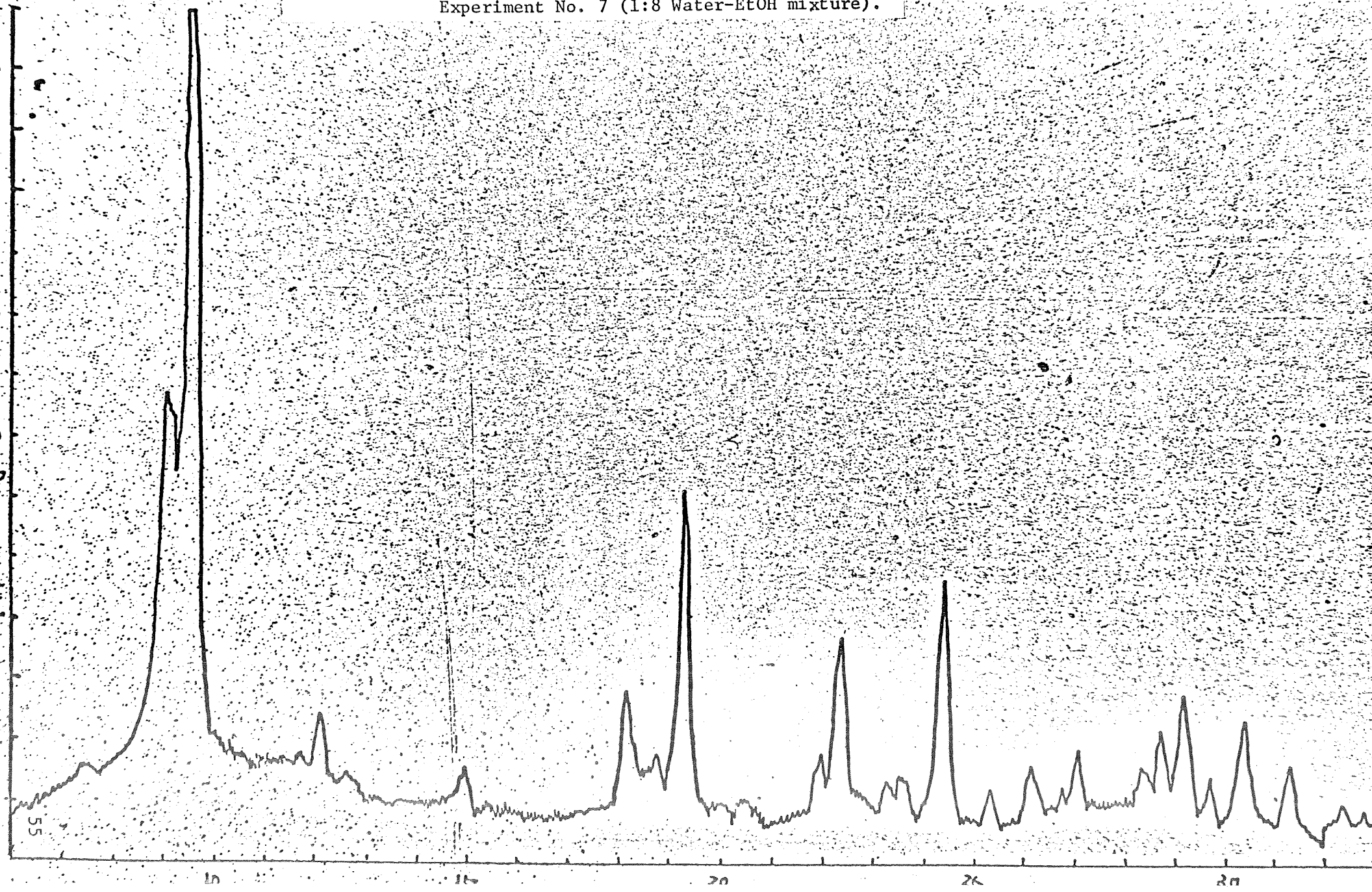


Figure 4-6. Powder X-ray analysis pattern.

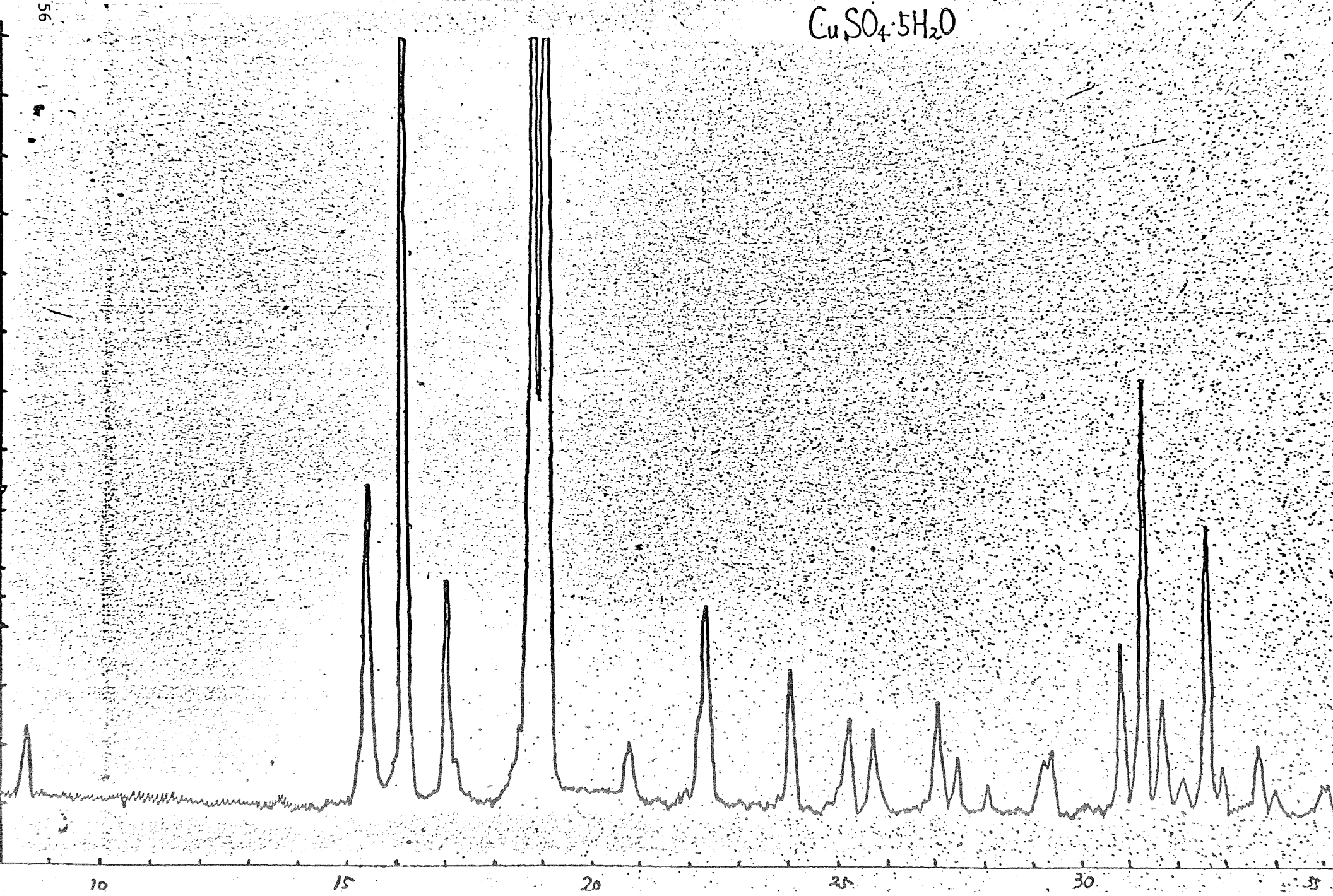


TABLE 5. RESULTS OF POWDER X-RAY DIFFRACTION MEASUREMENTS (WATER-EtOH PRODUCTS)

Exp. No. (mixture) / d(Å)	No.2 (1:1)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:8)	$CuSO_4 \cdot 5H_2O$
13.81		++				
13.37	+++					
9.72		+++		+	++	10.40 +
9.31		+++				
9.21			+++	+++	+++	
8.49	+					
7.31				+	+	
7.25			+			
7.02		+				
5.94		+				5.71 ++
5.63	+					5.47 +++
4.89				+	+	5.22 +
4.87		+				
4.85	++		+			
4.80		+				

(continued)

TABLE 5. RESULTS OF POWDER X-RAY DIFFRACTION MEASUREMENTS (WATER-EtOH PRODUCTS)

(continued)

Exp. No. (mixture) / d(Å)	No.2 (1:1)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:8)	$CuSO_4 \cdot 5H_2O$
4.72				+	+	4.72 +++
4.70			+			4.65 +++
4.41	+					
4.38	+					4.27 +
4.06		++	++			
3.99				++	++	3.99 +
3.95			++			
3.90	+					
3.80	+					
3.79		+				3.71 +
3.66				++	++	
3.65		+				
3.63			++			
3.52				+		3.55 +
3.50	+	+				3.45 +
3.41				+	+	

(continued)

TABLE 5. RESULTS OF POWDER X-RAY DIFFRACTION MEASUREMENTS (WATER-EtOH PRODUCTS)

(continued)

Exp. No. (mixture) / d(Å)	No.2 (1:1)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:8)	$CuSO_4 \cdot 5H_2O$
3.39		+				
3.38	++					
3.33			+			
3.30				+	+	3.30 +
3.23	+					3.25 +
3.13			+			3.17 +
3.11				+	+	
3.10			+			3.07 +
3.06		+	+			3.05 +
3.05		+		+	+	
3.01				+	+	
2.98			+			
2.94		+		+		
2.93			+			
2.90				+	+	2.90 +

(continued)

TABLE 5. RESULTS OF POWDER X-RAY DIFFRACTION MEASUREMENTS (WATER-EtOH PRODUCTS)

(continued)

Exp. No. (mixture) / d(Å)	No.2 (1:1)	No.4 (1:1.5)	No.5 (1:2)	No.6 (1:4)	No.7 (1:8)	$CuSO_4 \cdot 5H_2O$
2.86		+		+	+	2.86 ++
2.85		+				2.82 +
2.76			+			2.79 +
2.54			+			2.75 ++
2.43				+	+	2.72 +
2.42			+			2.66 +
2.36				+	+	2.64 +
2.35			+			2.56 +
2.29			+	+	+	2.53 +
2.28		+				2.40 +
2.21				+	+	2.36 +
2.20			+			2.33 +

peak strength +<++<+++ の sequence.

Figure 5-1. Differential heat balance analysis. (Experiment No. 2) Mixture (1:34 Water-EtOH).

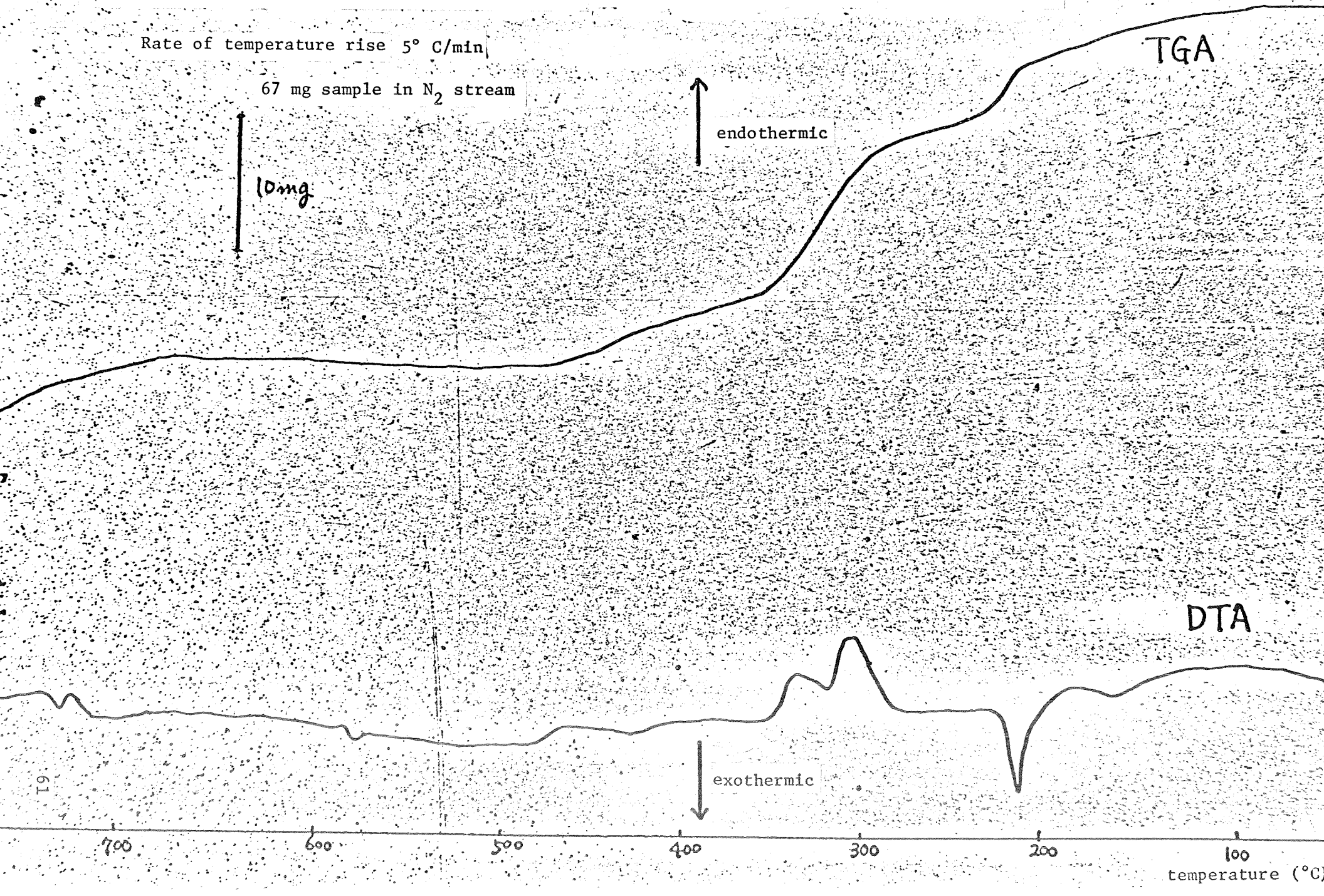


Figure 5-2. Differential heat balance analysis.

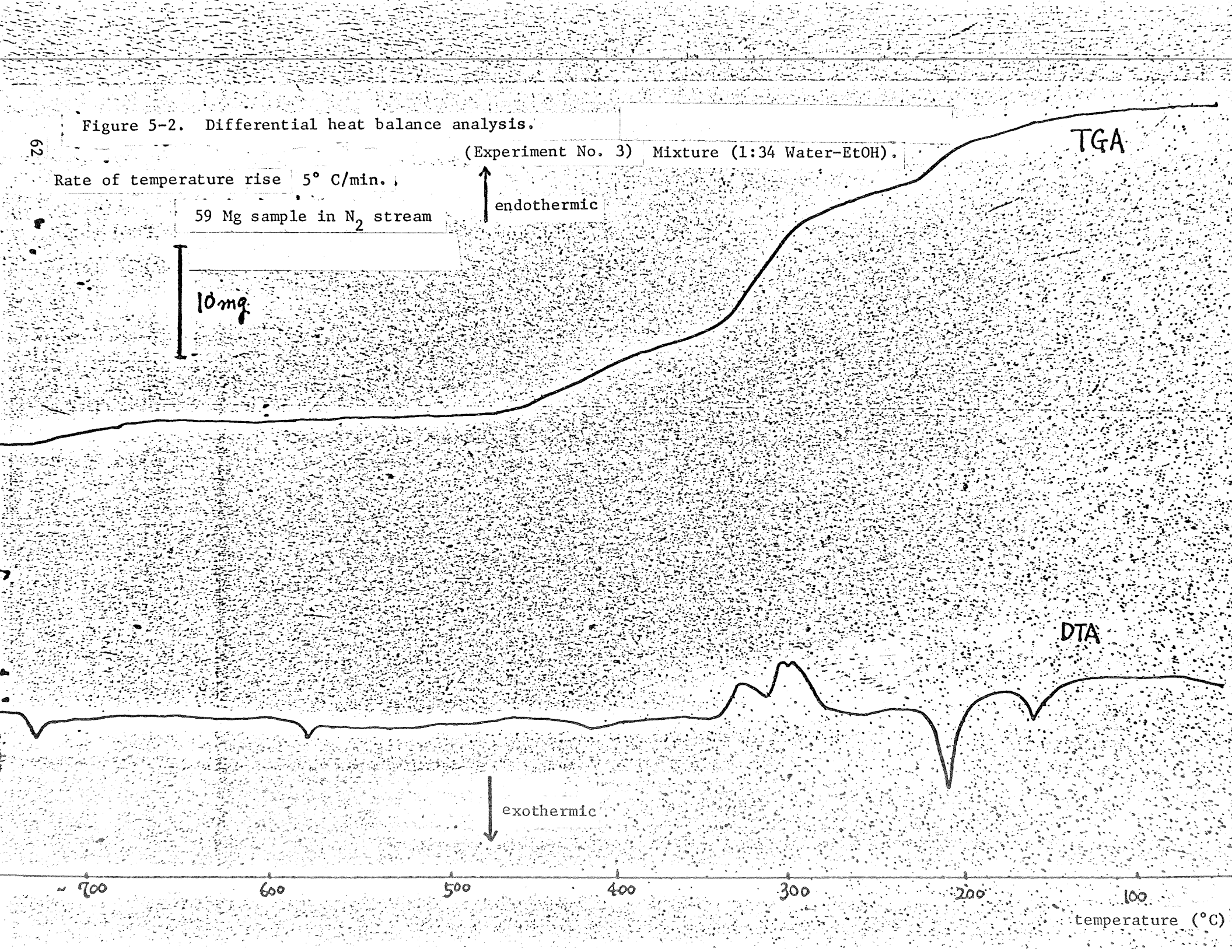


Figure 5-3. Differential heat balance analysis. (Experiment No. 4) (1:1.5 Water-EtOH)

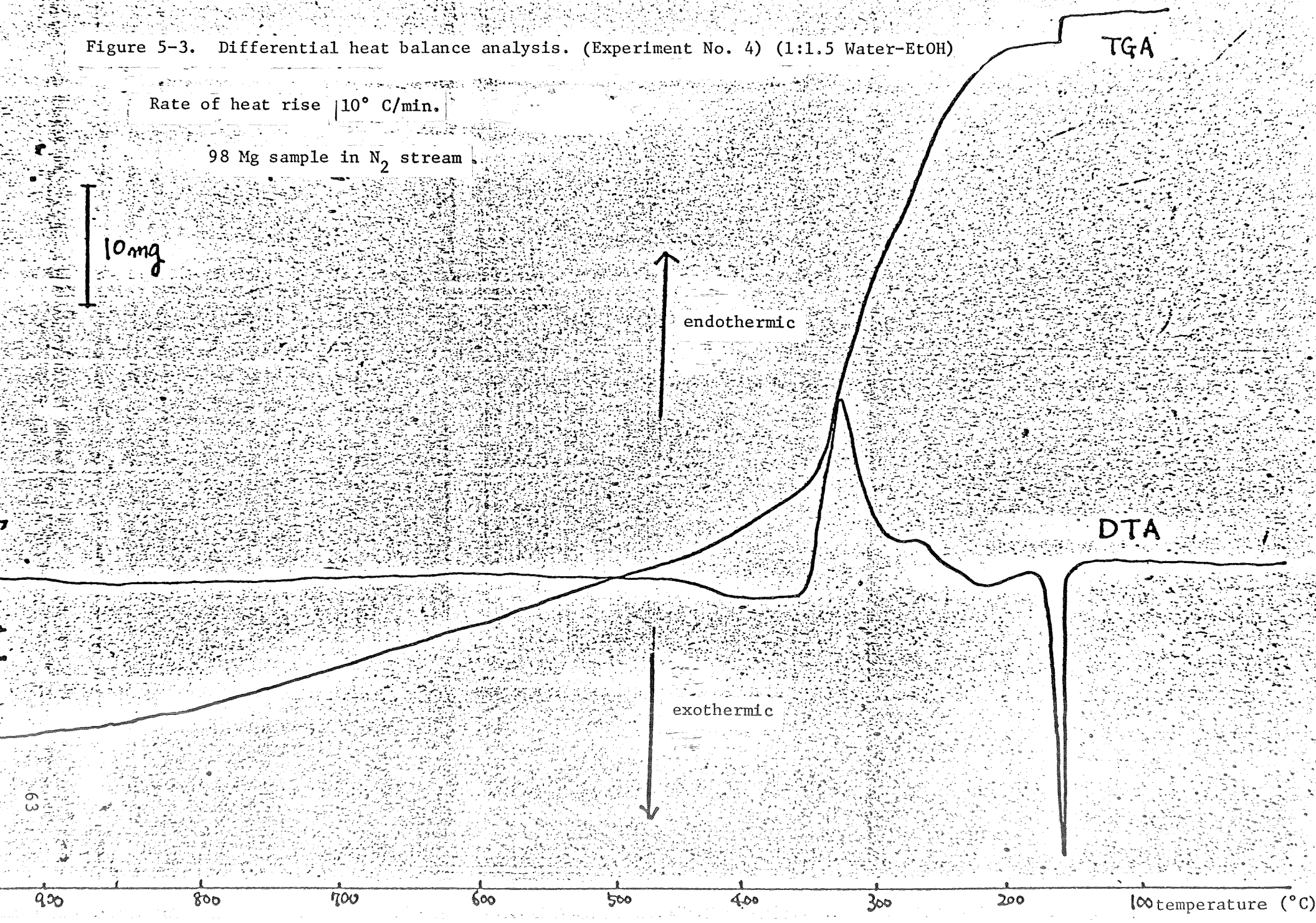


Figure 5-4. Differential heat balance analysis. (Experiment No. 5) (1:2 Water-EtOH)

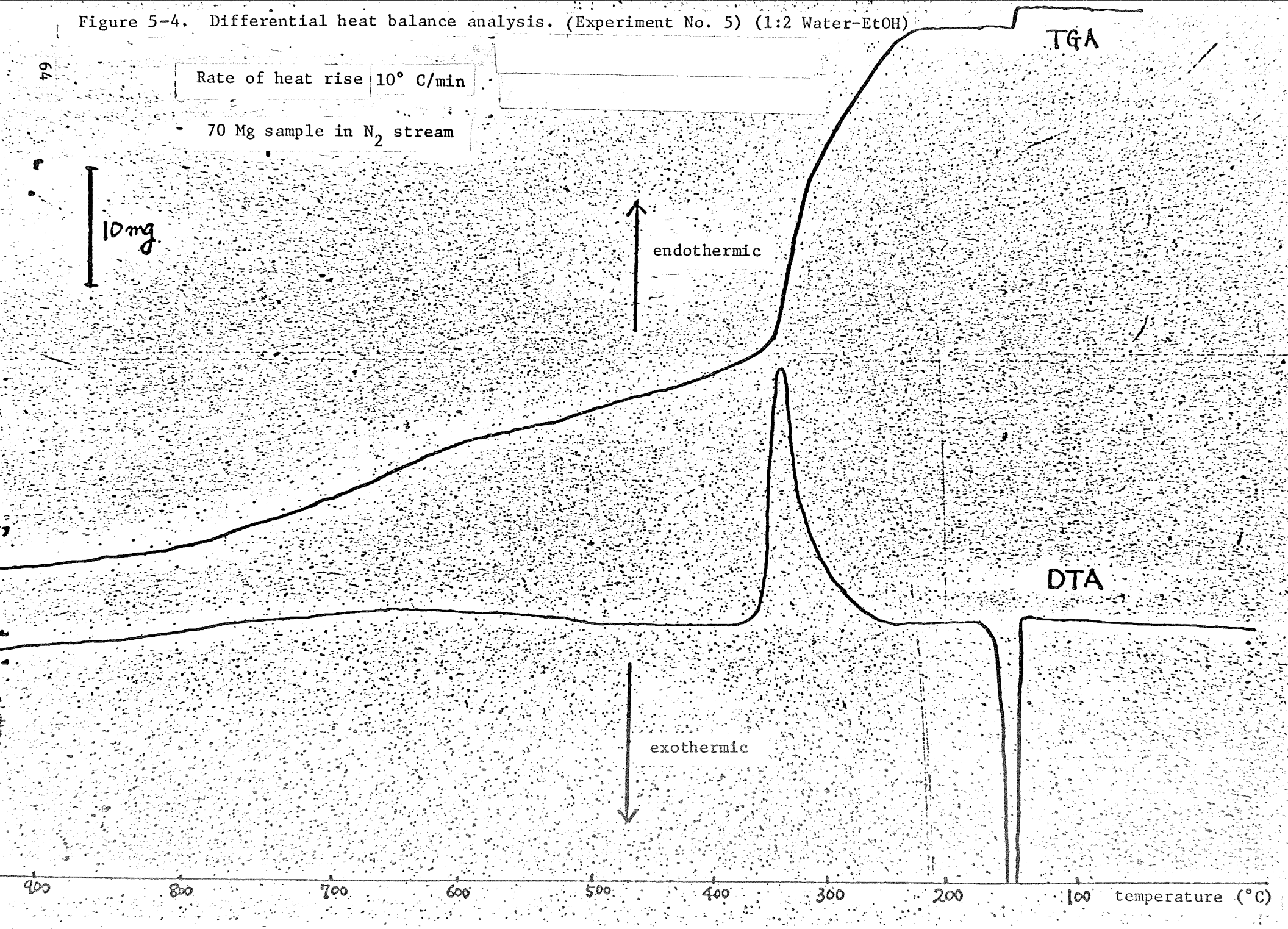


Figure 5-5. Differential heat balance analysis. (Experiment No. 6) (1:4 Water-EtOH).

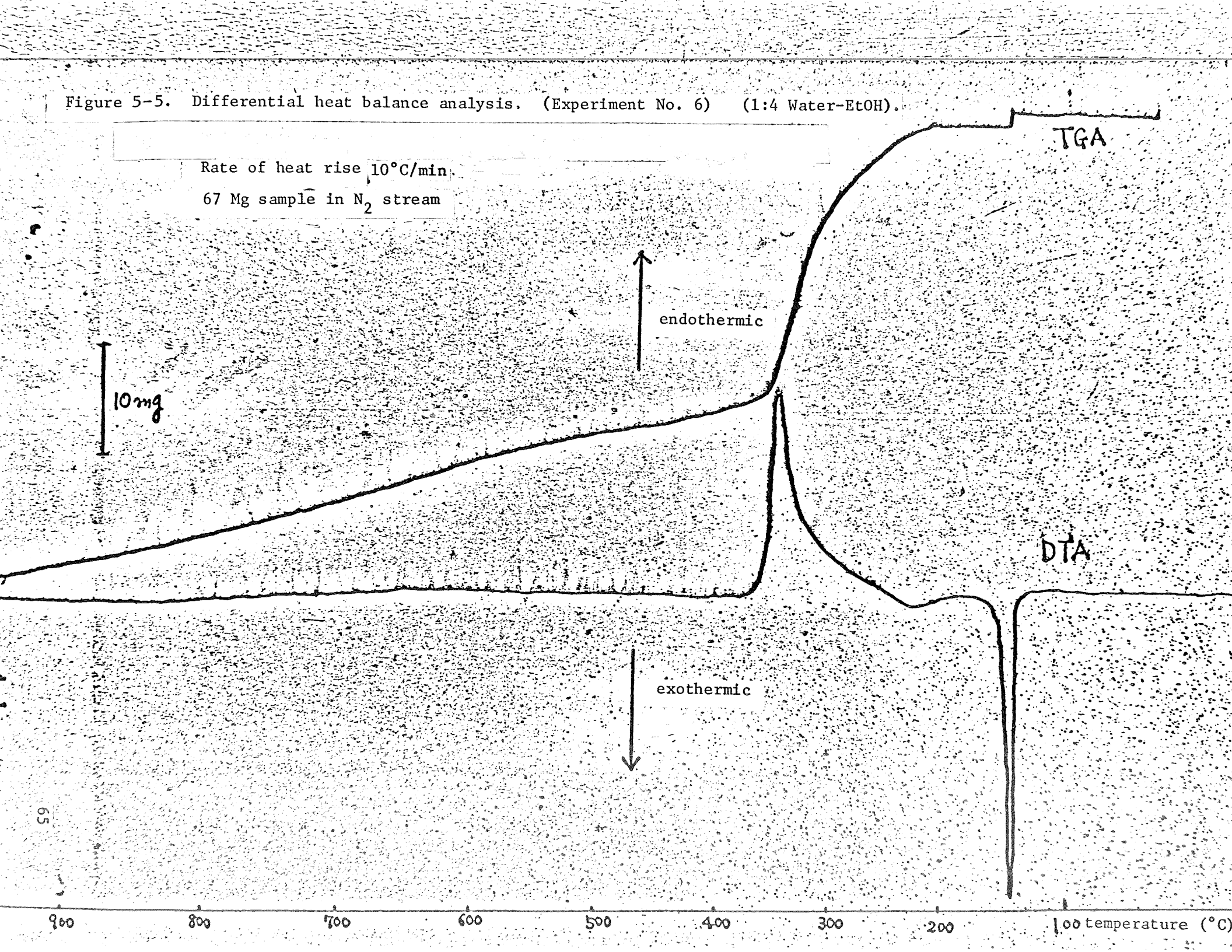


Figure 5-6. Differential heat balance analysis. (Experiment No. 7) (1:8 Water-EtOH)

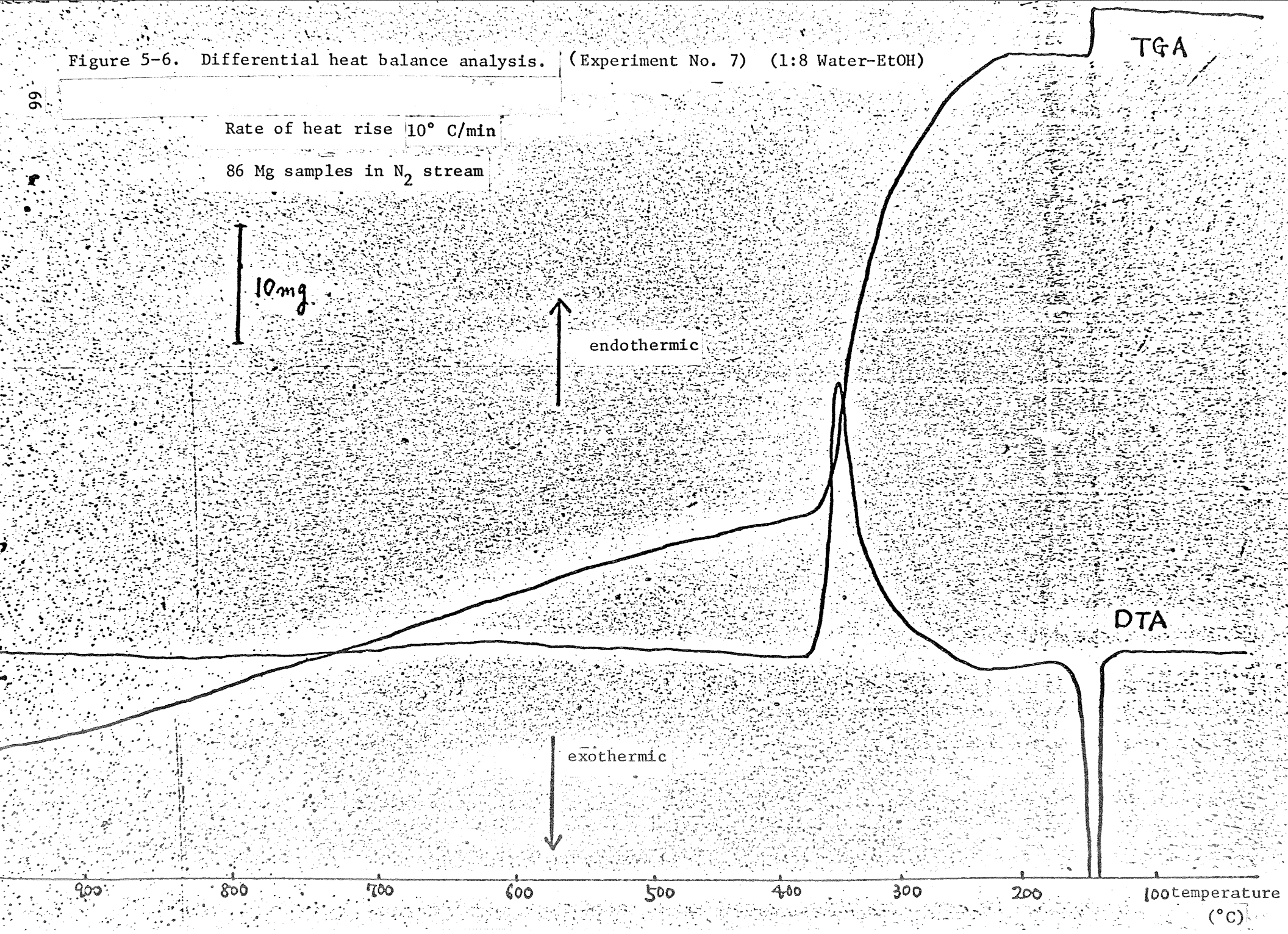


TABLE 6. RECOVERY OF COORDINATORS FROM CHAINS

(Water-EtOH products)

Experiment No.	Mixture ratio $\frac{CuSO_4}{AAN\text{-}AcOH}$	$\frac{AAN}{Cu}$	$\frac{Gly\text{-}NH_2}{Cu}$	SUM	
				$\frac{AAN+Gly\text{-}NH_2}{Cu}$	$\frac{2(AAN+Gly\text{-}NH_2)}{total\ N}$
1	1:0.5	0.054	0.347	0.401	(140)
2	1:1	0.272	0.214	0.486	100
3	1:1.34	0.368	0.130	0.498	77
4	1:1.5	0.798	0.098	0.896	88
5	1:2	1.746	0.088	1.834	100
6	1:4	2.02	—	2.02	98
7	1:8	1.91	—	1.91	97

$Gly\text{-}NH_2$ indicates glycyl amides

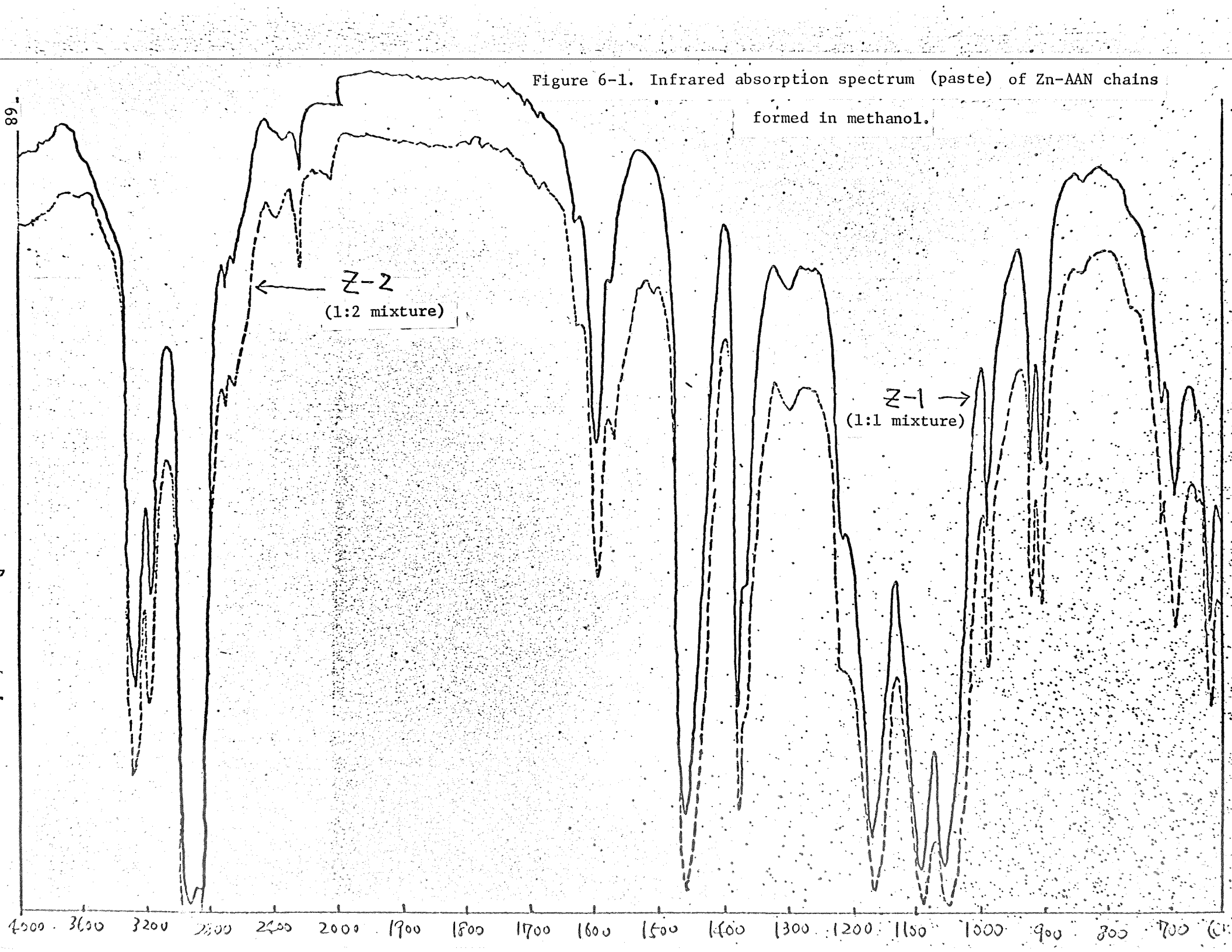


Figure 6-1. Infrared absorption spectrum (paste) of Zn-AAN chains formed in methanol.

Figure 6-2. Infrared absorption spectrum of Zn-AAN chains formed in methanol.

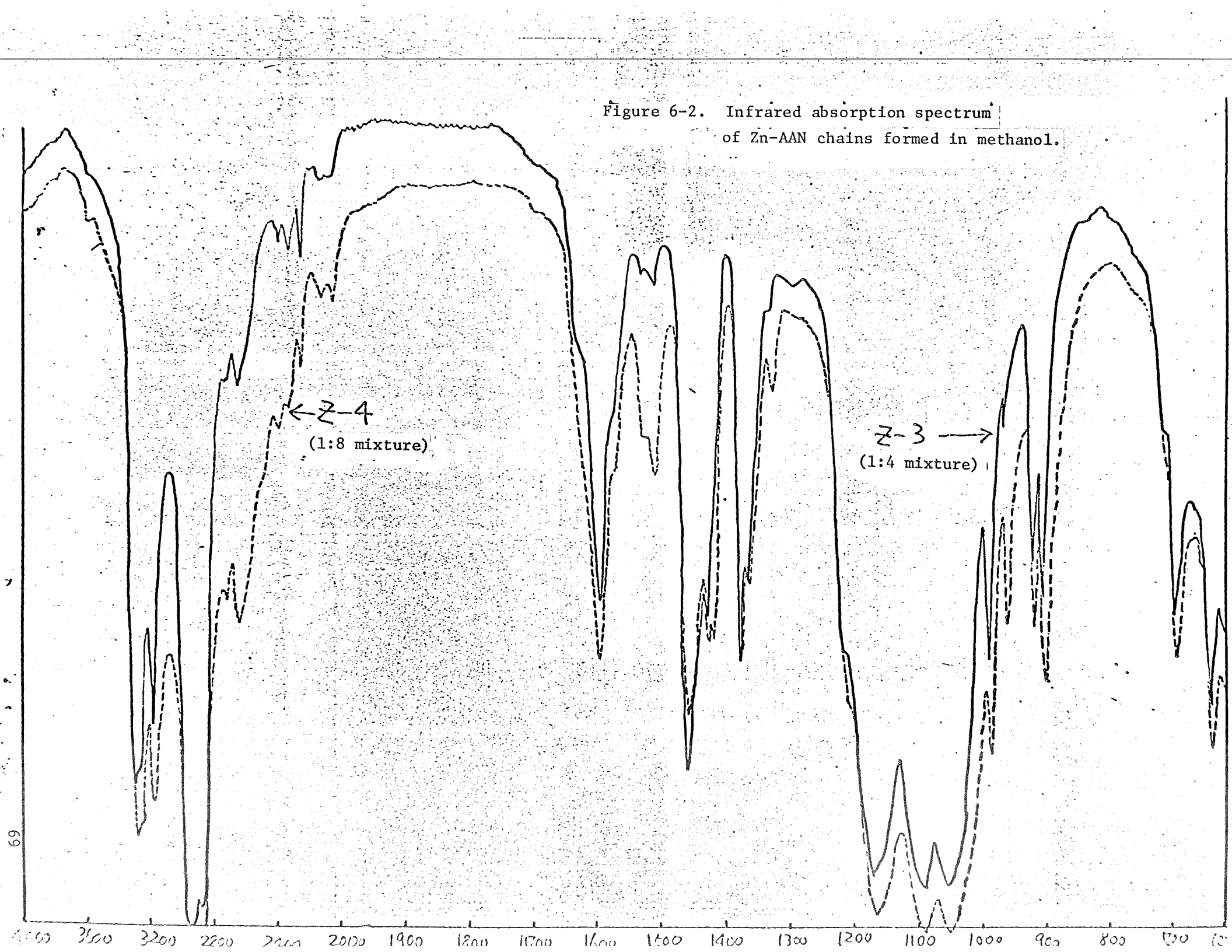


TABLE 7. RESULTS OF DIFFERENTIAL HEAT ANALYSIS OF AMINOACETONITRILE COPPER CHAINS (FORMED IN WATER-EtOH) (1)

Sample	Outline of Analysis Results
No. 2 (1:1 mixture) Heat rise 5° C/min	(1) Slightly exothermic near 160° C. Slightly exothermic at 208° — 5.97% weight loss. (2) Slightly endothermic peaks at 270° - 360° C and at 308° C and 324° C. 16.26% weight loss in between. (3) Subsequent gradual weight loss. Total weight loss 60.74 % near 970° C.
No. 3 (1:1.34 mixture) Heat rise 5° C/min.	(1) Slightly exothermic with peaks at 150° C and 205° C. 11.7% weight loss in between. (2) Slightly exothermic peaks at 270° - 320° C and at 305° C and 330° C with 16.44% weight loss in between. (3) Subsequent gradual weight loss. Total weight loss 54.9% near 970° C.
No. 4 (1:1.5 mixture) Heat rise 10° C/min.	(1) Sharply exothermic at 150° C accompanied by sharp 2.34% weight loss. (2) Greatly endothermic from 220° to 370° C. 36.43% weight loss in between. (3) Gradual weight loss near 970° C. Total weight loss 60.92%.
No. 5 (1:2 mixture) Heat rise 10° C/min.	(1) Sharply exothermic at 150° C accompanied by 2.86% weight loss. (2) Greatly endothermic from 250° - 370° C with 38.71% weight loss. (3) Subsequent gradual weight loss. Total weight loss 68.29% near 970° C.
No. 6 (1:4 mixture) Heat rise 10° C/min	(1) Sharply exothermic at 140° C, with 2.58% weight loss. (2) Greatly endothermic from 230° - 370° C with 39.22% weight loss in between. (3) Subsequent gradual weight loss. Total weight loss 66.6% at 970° C.

(Continued)

TABLE 7. RESULTS OF DIFFERENTIAL HEAT ANALYSIS OF AMINOACETONITRILE COPPER CHAINS (FORMED IN WATER-EtOH) (1)

Sample	Outline of Analysis Results
No. 7 (1:8 mixture) Heat rise 10° C	(1) Sharply exothermic at 140° C with sharp 4.53% weight loss. (2) Endothermic between 230° and 370° C, with 44.4% weight loss. (3) Subsequent gradual weight loss. Total weight loss 71.8% near 970° C.

(Concluded)

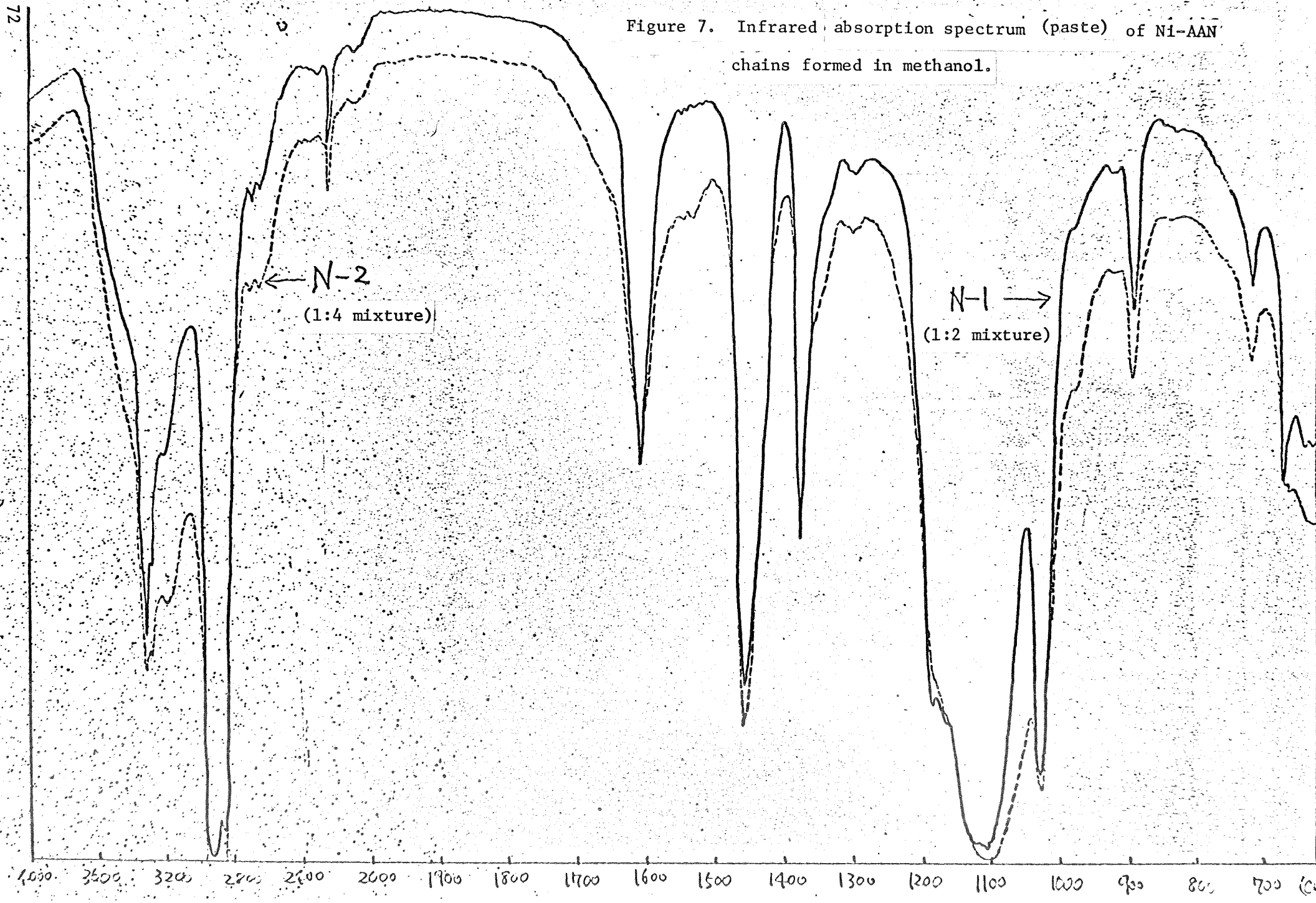


Figure 7. Infrared absorption spectrum (paste) of Ni-AAN chains formed in methanol.

TABLE 8. REACTION PRODUCTS OF AMINOACETONITRILE ACETATE AND $ZnSO_4$-$7H_2O$ IN METHANOL

Exp. No.	Reagent			Element analysis values					yield	color
	$ZnSO_4 \cdot 7H_2O$ mol/cc (X)Hv	AAN·AcOH mol/cc (X)Hv	Zn/AAN	H %	C %	N %	Zn^a %	Zn^b %	gr	
Z-1	0.005/25	0.005/20	1:1	2.73	16.99	19.72	22.88	23.51	0.3597	白色
Z-2	0.005/20	0.01/10	1:2	2.97	17.47	19.55	( )	23.61	1.2172	〃
Z-3	0.005/20	0.02/20	1:4	3.01	17.79	20.49	20.95	20.49	1.1195	〃
Z-4	0.0025/20	0.02/20	1:8	3.25	18.86	21.66	16.54	17.36	0.5748	〃
Z-5	0.0025/20	0.025/30	1:10	2.87	17.69	20.45	22.14	21.48	0.4614	うすい褐色

Zn^a calculated from element analysis ash

Zn^b theoretical value from element analysis by chelate titration

	Zn	H	C	N	SO_4	O
$Zn(AAN)_2SO_4$	23.27	2.95	17.56	20.48	35.11	
$Zn(AAN)_3SO_4$	19.83	3.67	21.86	25.49	29.14	
$Zn(AAN)_4SO_4$	16.75	4.18	24.91	29.05	24.91	

Figure 8. Infrared absorption spectrum (paste) of Co-AAN chains formed in methanol.

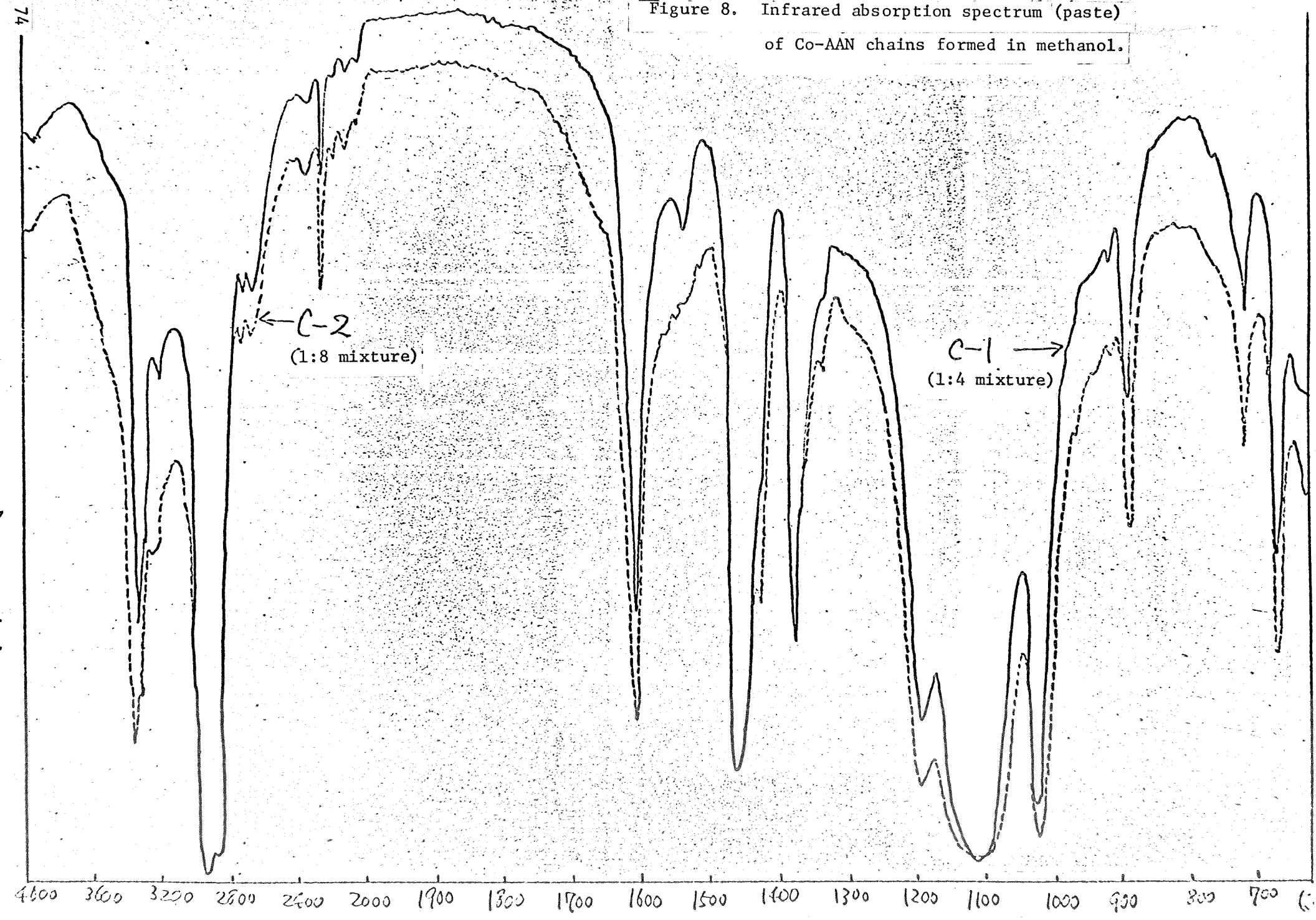


TABLE 9. REACTION PRODUCTS OF AMINOACETONITRILE ACETATE AND $NiSO_4 \cdot 6H_2O$ IN METHANOL

Exp. No.	Reagent			Element analysis values				Yield	Color
	$NiSO_4 \cdot 6H_2O$ mol/cc	AAN·AcOH mol/cc	Ni/AAN	H %	C %	N %	Ni %	gr	
N-1	0.005/10	0.01/15	1:2	3.20	16.83	19.52	21.02	0.7559	pale green
N-2	0.0025/15	0.015/15	1:6	4.01	17.62	20.20	19.00	0.3641	"
N-3	0.0025/50	0.02/20	1:8	3.57	17.23	19.89	21.07	05191	"

theoretical element analysis values

	Ni	H	C	N	SO_4	O
$Ni(AAN)_2SO_4$	22.00	3.02	18.00	20.99	35.99	
$Ni(AAN)_2SO_4 \cdot H_2O$	20.61	3.54	16.86	19.66	33.72	5.62

Figure 9. Chromatograms of amino acid analyses for coordinator reactions

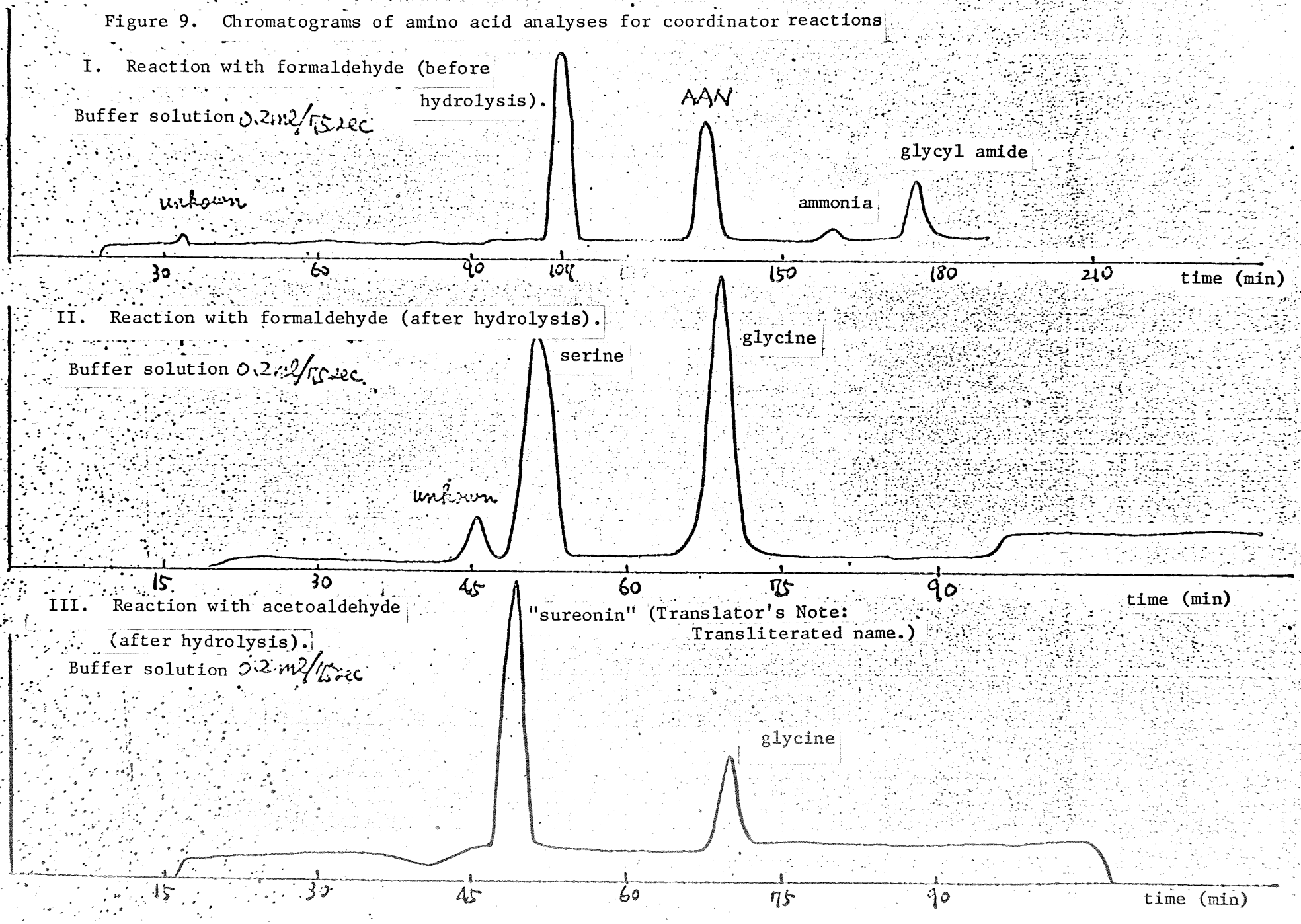


TABLE 10. REACTION PRODUCTS OF AMINOACETONITRILE ACETATE AND $CaSO_4 \cdot 7H_2O$ IN METHANOL

Exp. No.	Reagent			Element analysis values				Yield	Color
	$CoSO_4 \cdot 7H_2O$ mol/cc	AANAcOH mol/cc	Co/AAN	H %	C %	N %	Co %	g	
C-1	0.005/20	0.02/20	1:4	2.97	18.17	20.88	20.78	1.0468	pink
C-2	0.0025/15	0.02/20	1:8	2.98	18.13	20.63	19.96	0.5228	〃

theoretical element analysis values

	Co	H	C	N	SO_4	O
$Co(AAN)_2SO_4$	22.06	3.02	19.99	20.97	35.96	
$Co(AAN)_2SO_4 \cdot H_2O$	20.64	3.53	16.85	19.65	33.69	5.61

Figure 10. Chromatograms from amino acid analyzer of coordinator reactions.

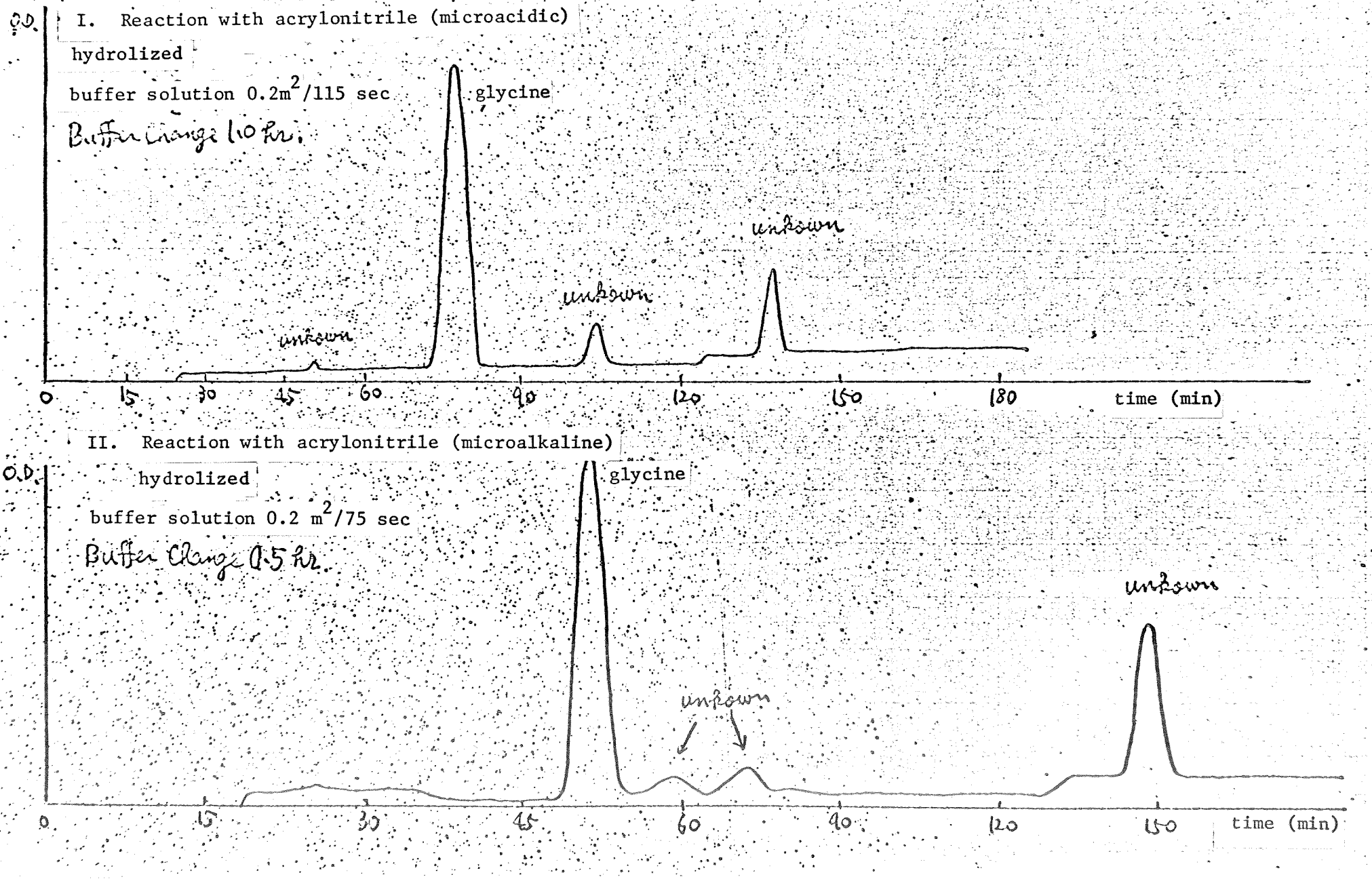


TABLE 11. RETENTION TIMES FOR TMS SUGARS

column temperature 175°C N_2 = 40 ml/min column 6% SE-30 3m

TMS Compounds	Retention time	Comparative retention time
TMS-L- sorbose	11.8 (min)	0.91
TMS-α-D- glucose	12.9	1.00
TMS-D- sorbitol	16.7	1.29
TMS-β-D- glucose	19.4	1.50
TMS-D- fructose	*	0.77

Retention time for TMS-alpha-D glucose is 1.00.

* Found from separate experiments.

column temperature 180°C N_2 = 20 ml/min column 5% H.V. silicon grease 3m

TMS Compound	Retention time	Comparative retention time
TMS-L- sorbose	12.2 (min)	0.91
TMS-α-D- glucose	13.4	1.00
TMS-D- sorbitol	17.0	1.27
TMS-β-D- glucose	19.6	1.46

Retention time for TMS-alpha-D glucose is 1.00.

Figure 11. Separation of TMS sugars by gas chromatography.

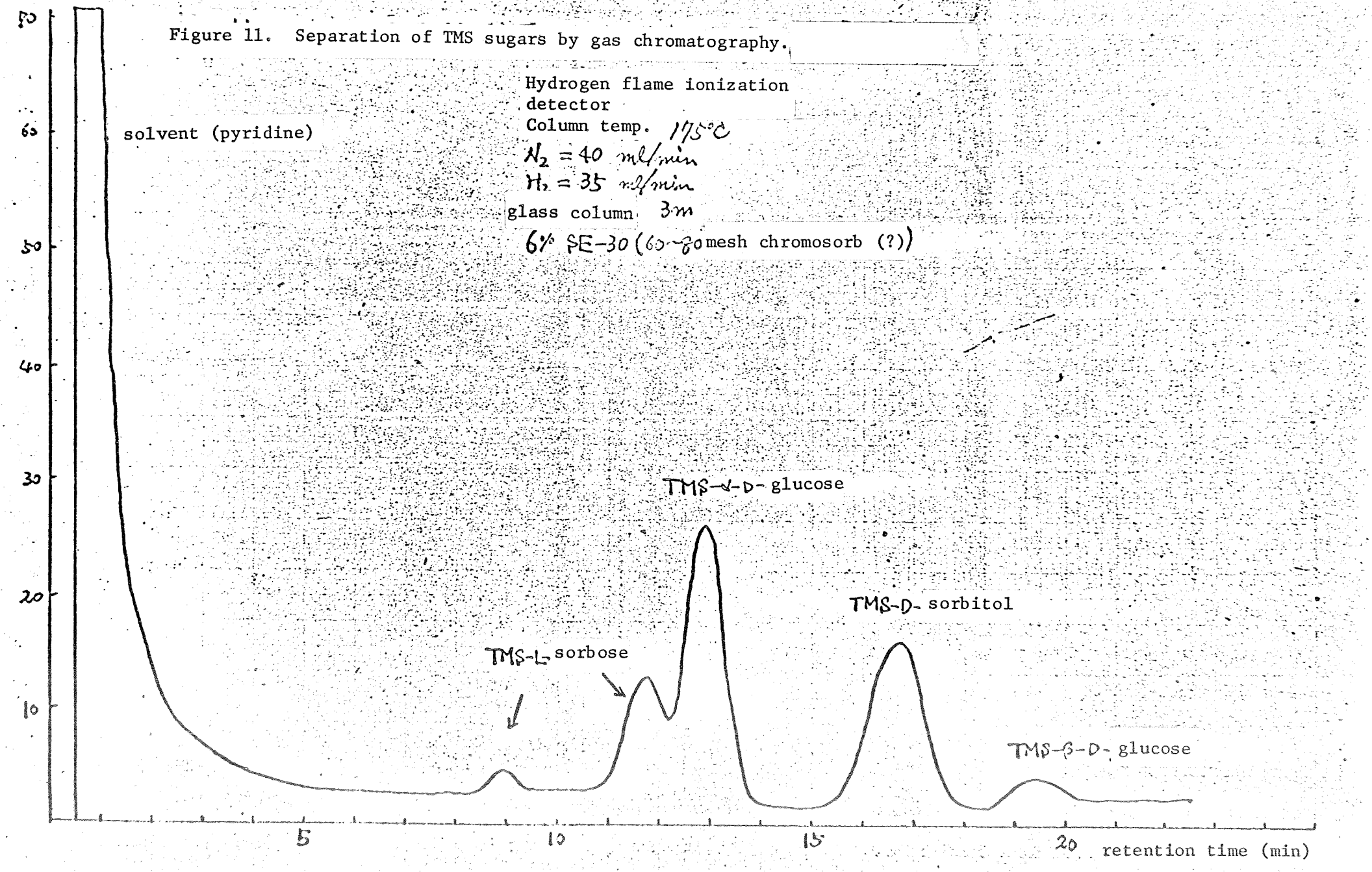


Figure 12. Separation of TMS sugars by gas chromatogram.

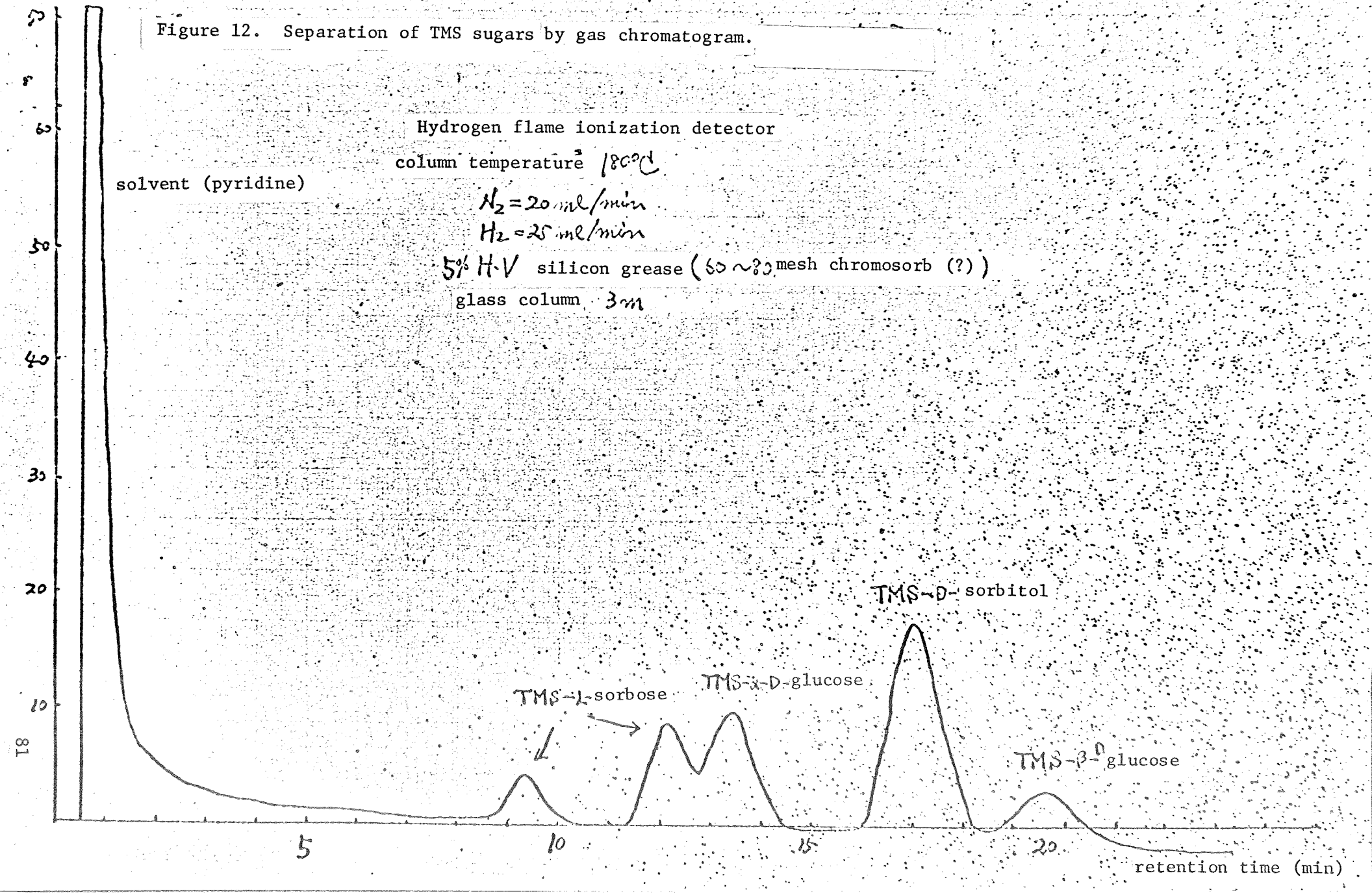


Figure 13. Gas chromatography for oxide products.

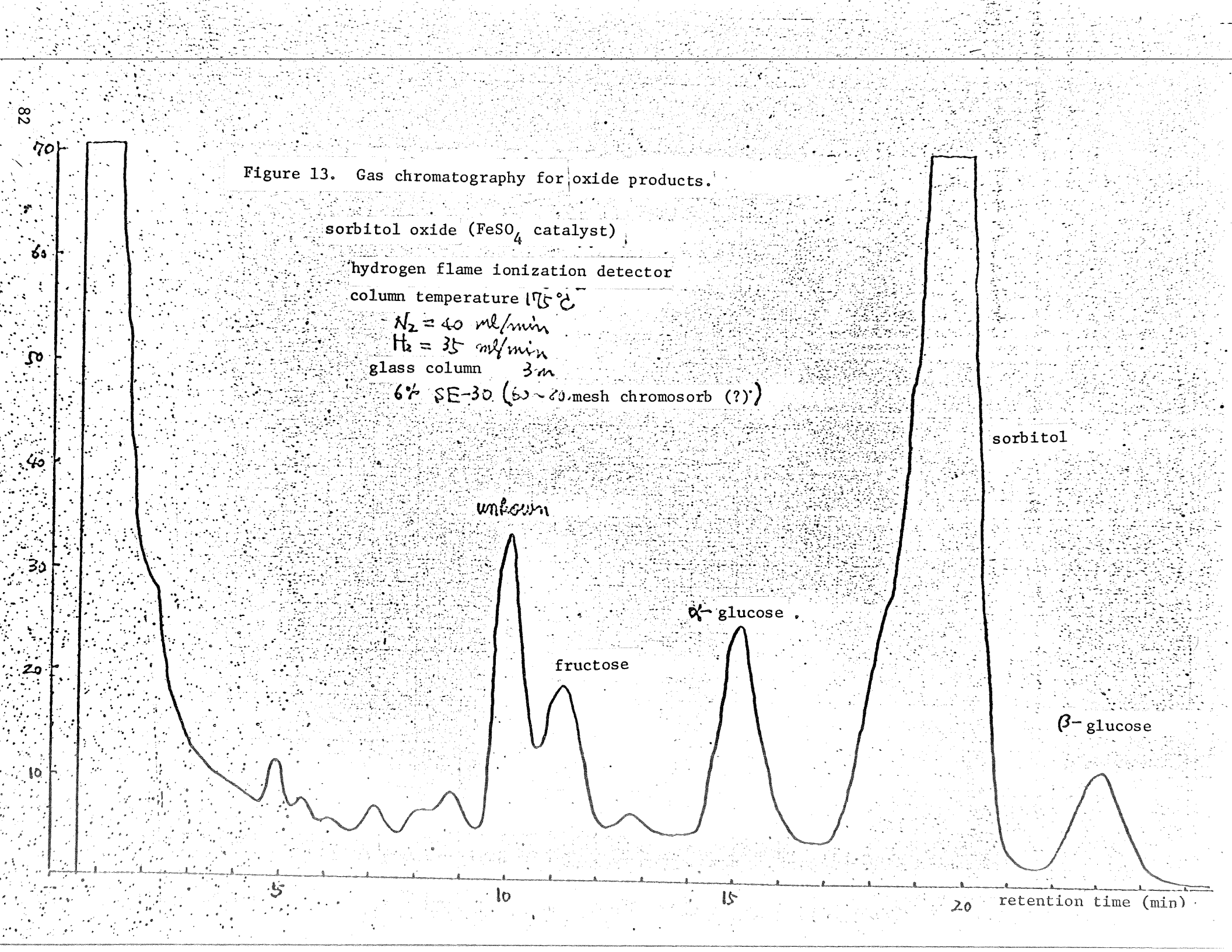


Figure 14. Gas chromatography for oxide products.

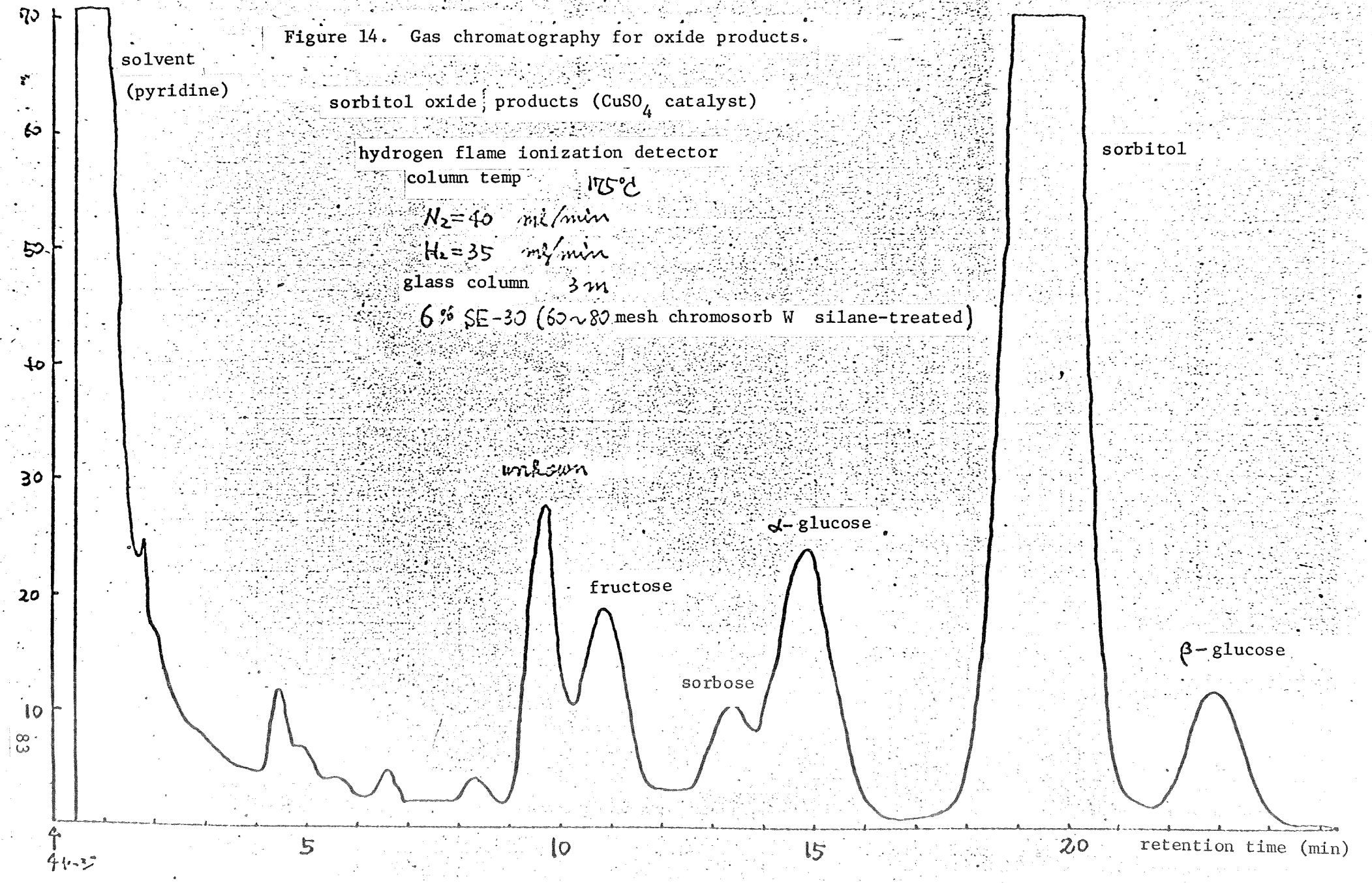


Figure 15. Gas chromatography for oxide products.

sorbitol oxide ($Cu\text{-}AAN_2SO_4$ catalyst)

hydrogen flame ionization detector

column temp 175°C

N_2 = 40 ml/min

H_2 = 35 ml/min

6% SE-30 (60~80 mesh chromosorb W (?))

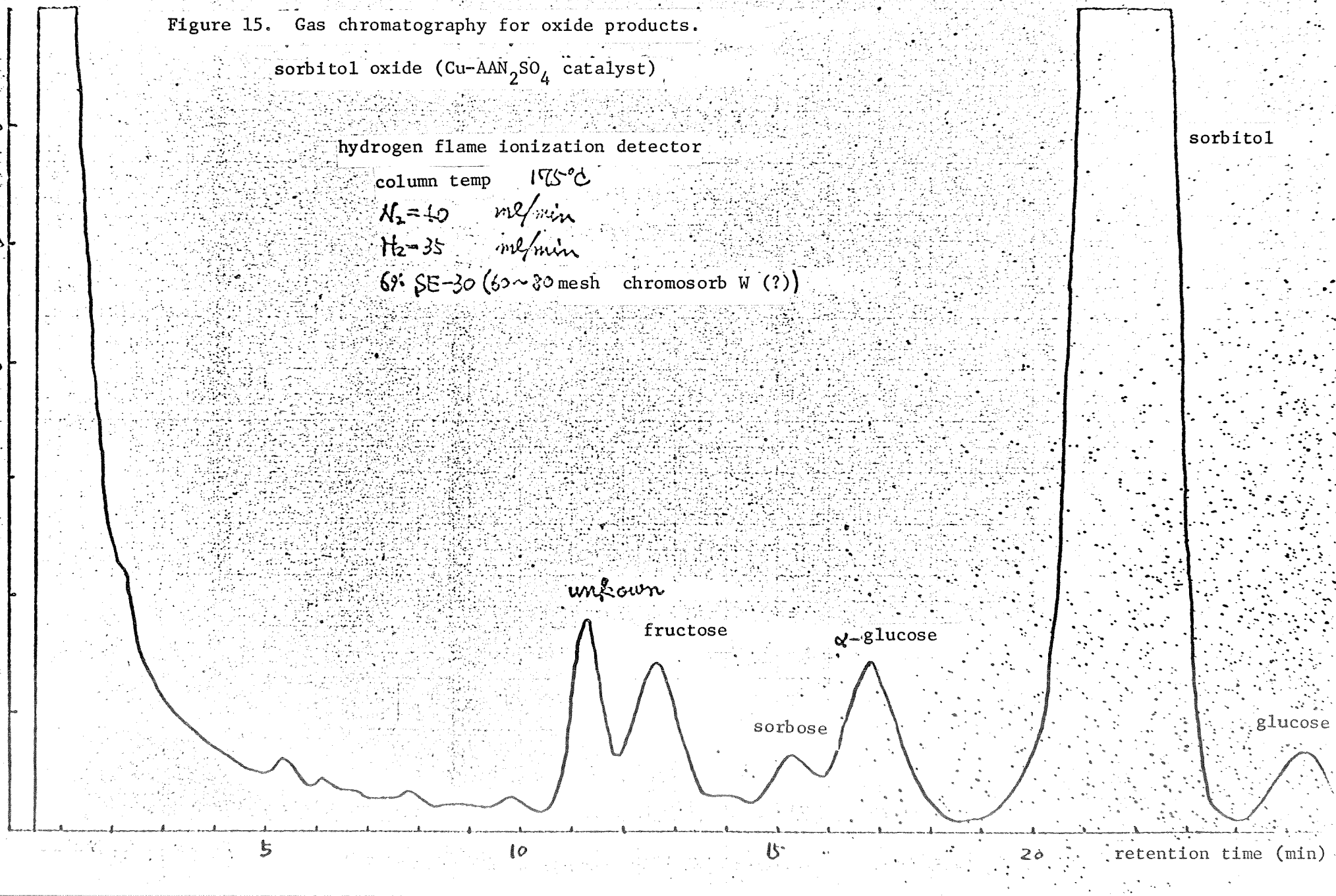


Figure 16. Gas chromatography for oxide products

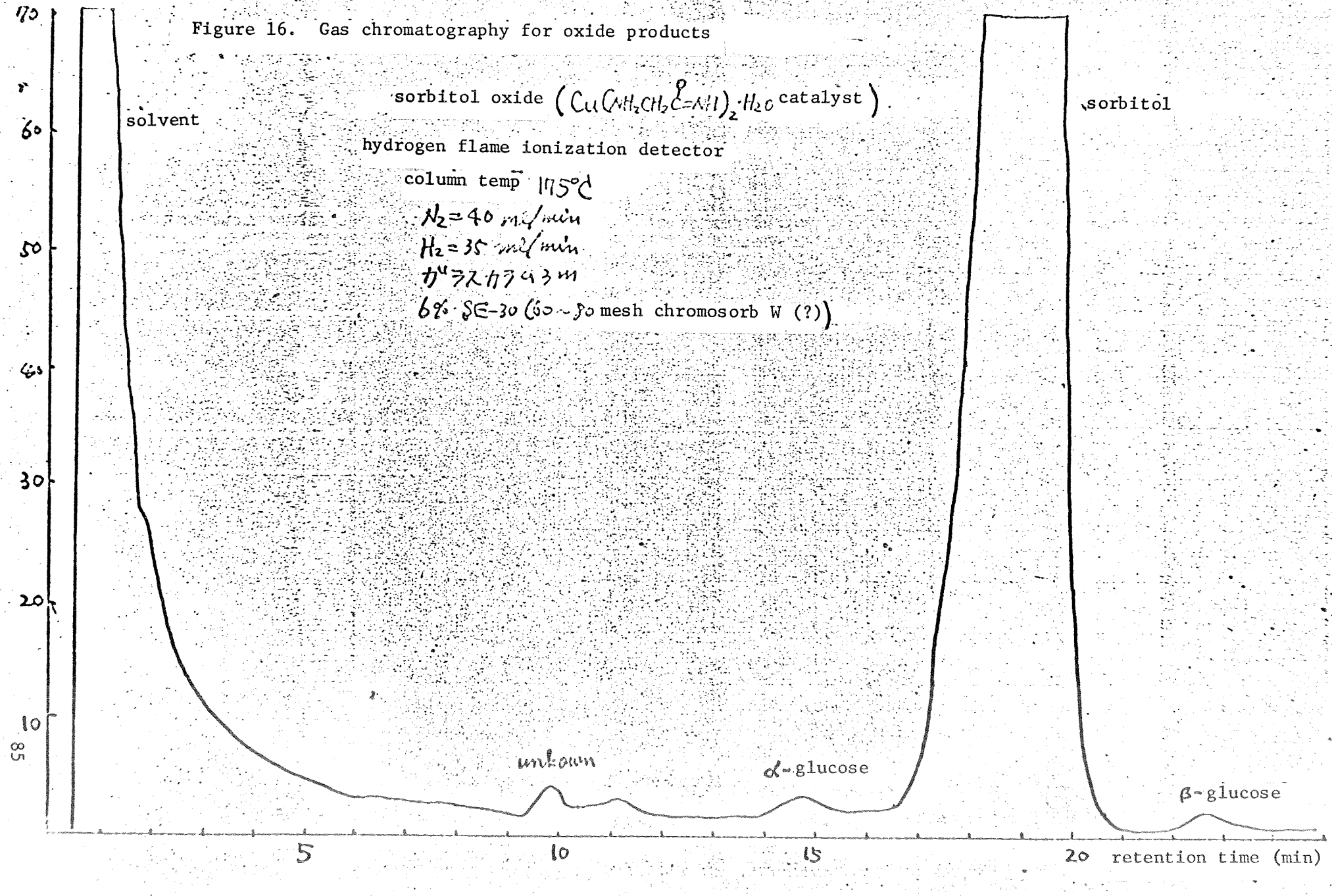
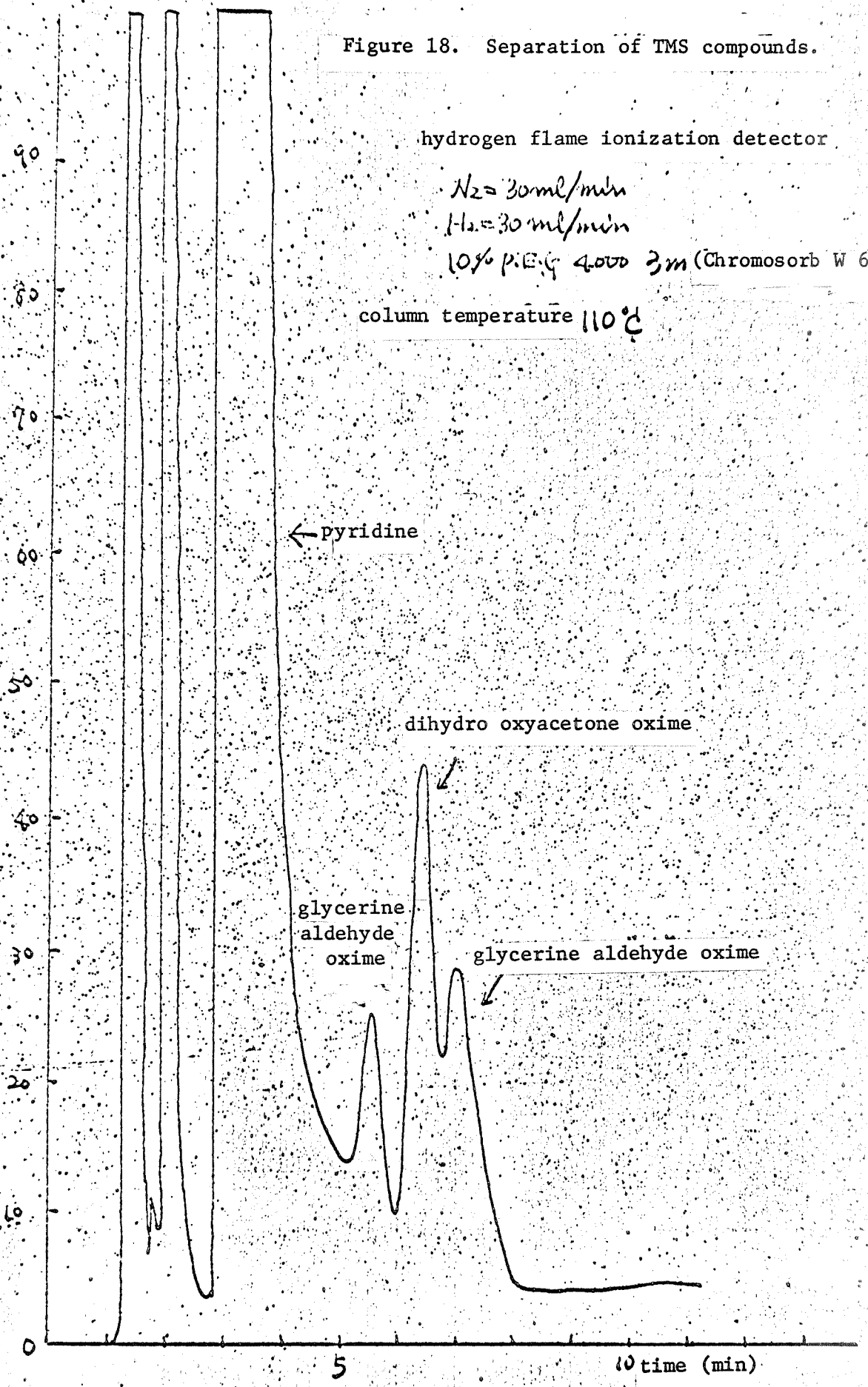


Figure 18. Separation of TMS compounds.



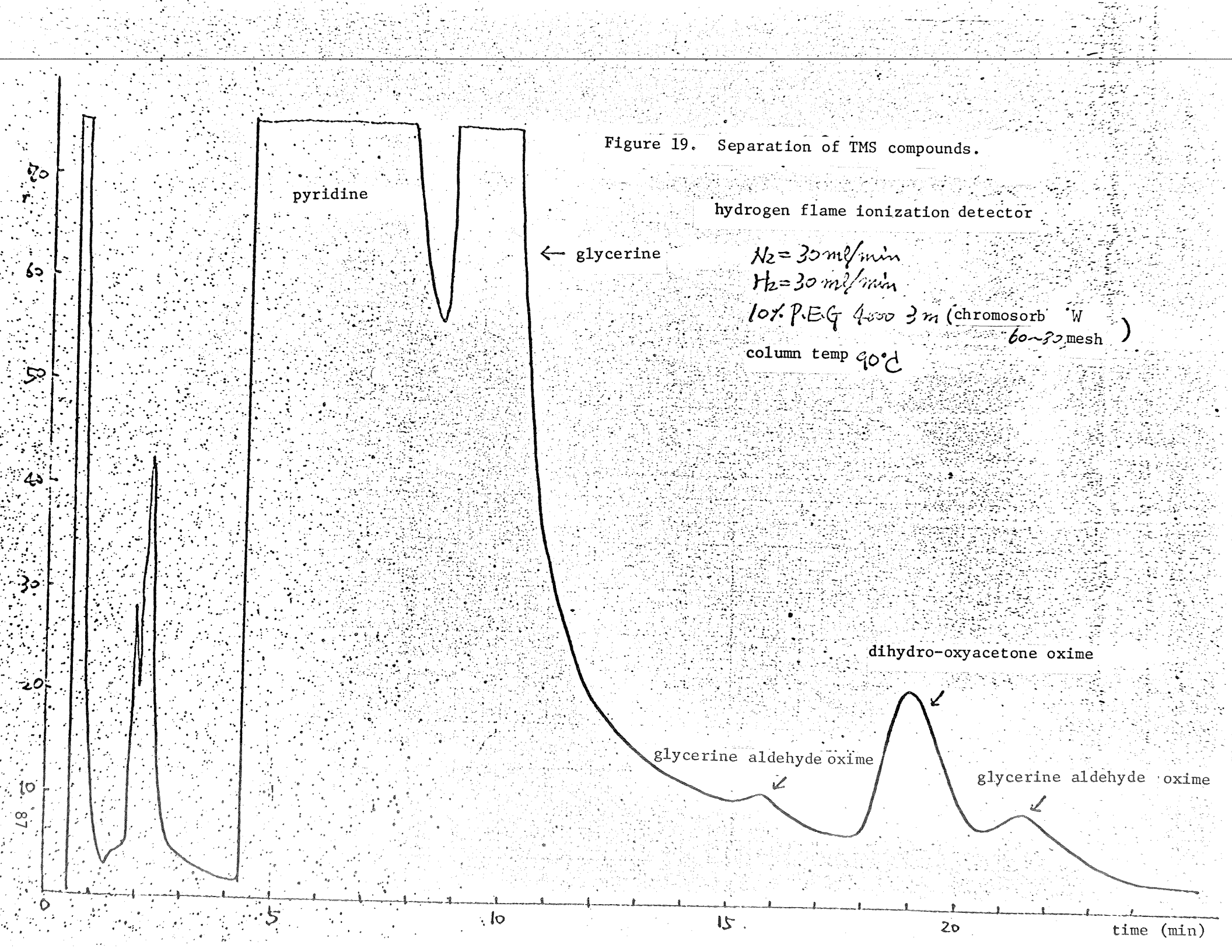


Figure 19. Separation of TMS compounds.

Figure 20. Glycerine oxide (catalyst $FeSO_4$)

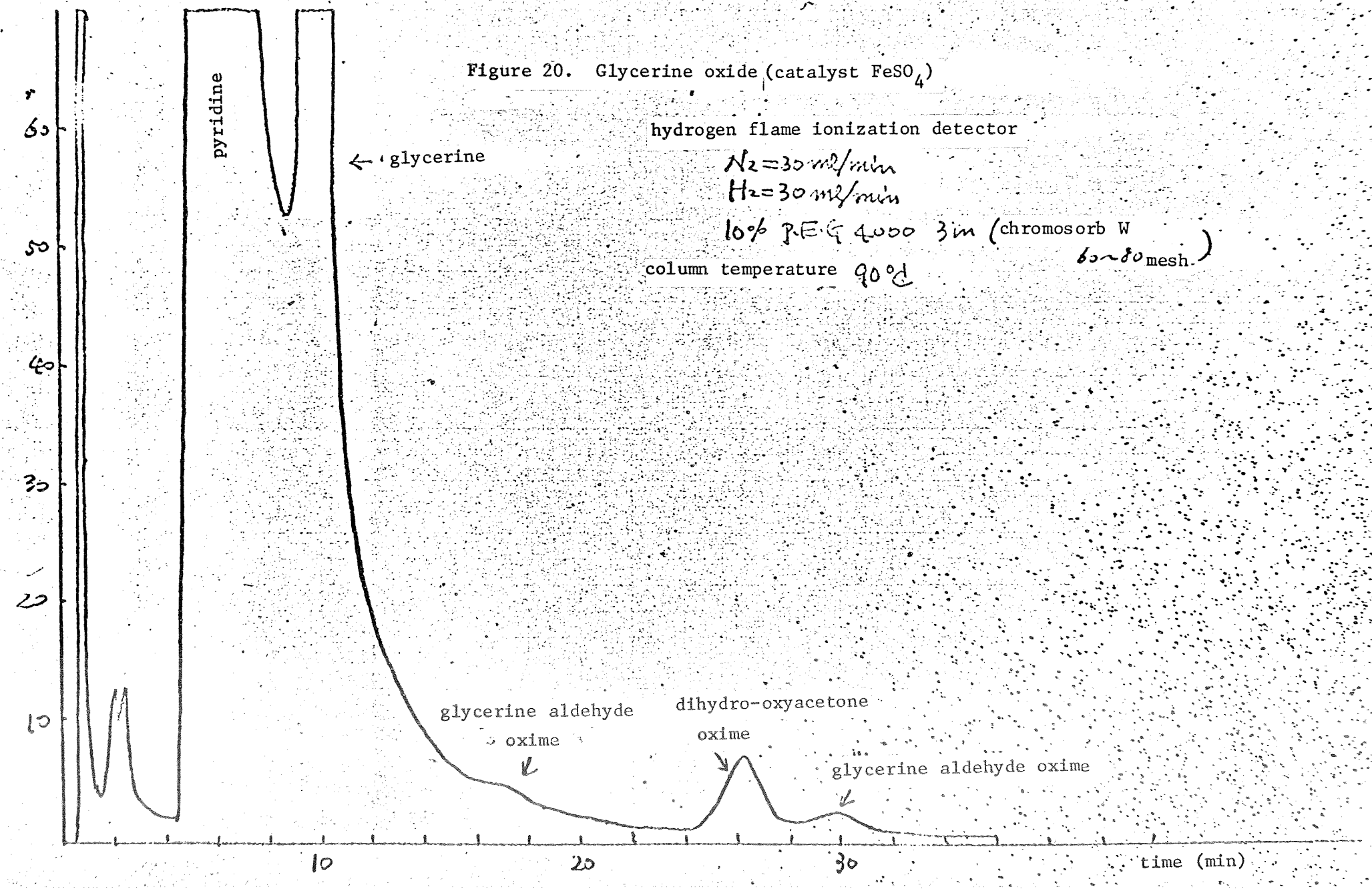
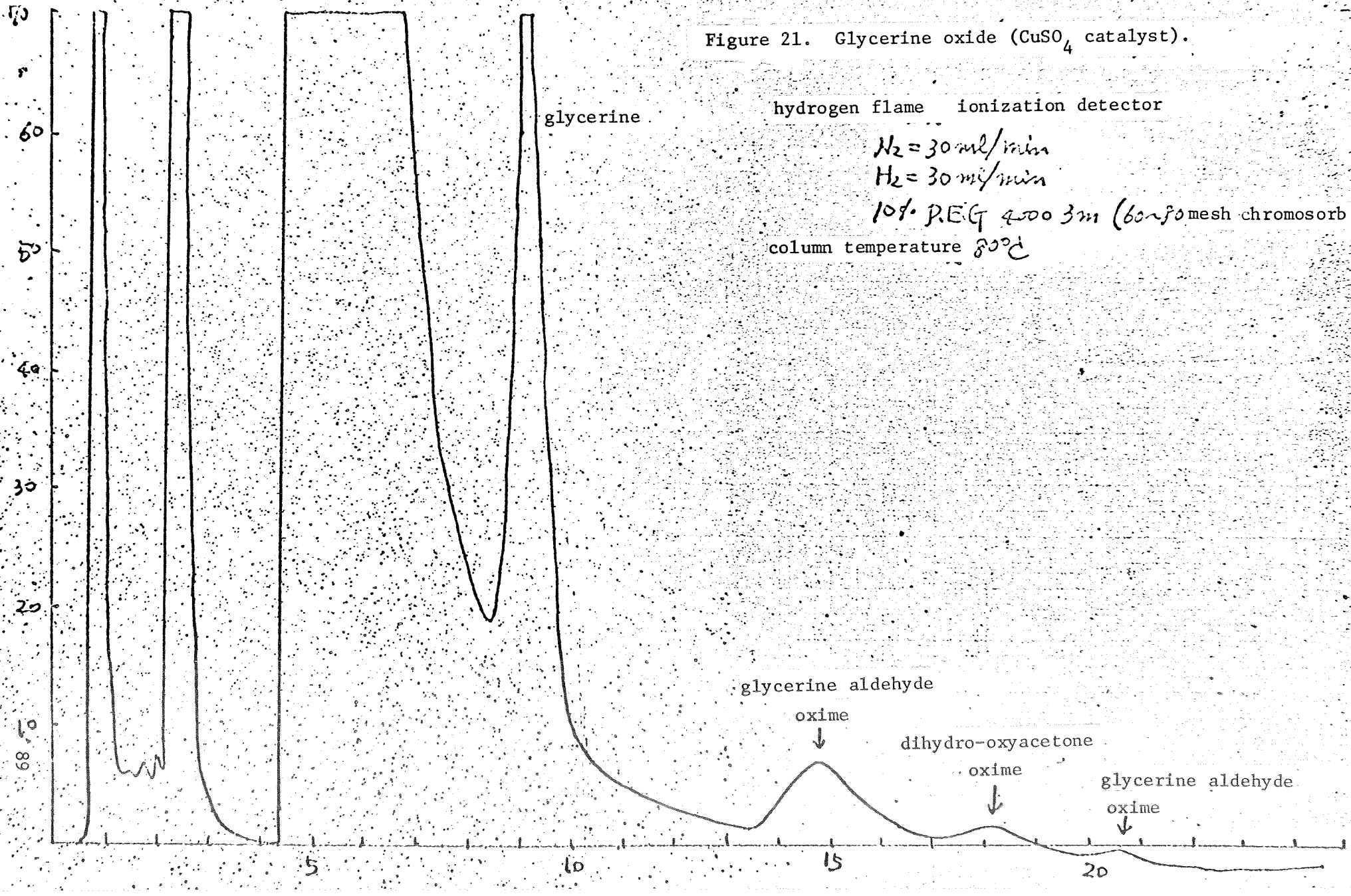


Figure 21. Glycerine oxide ($CuSO_4$ catalyst).



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